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The Journal
of the
SOCIETY OF DYERS AND COLOURISTS

Volume 67 Number 2

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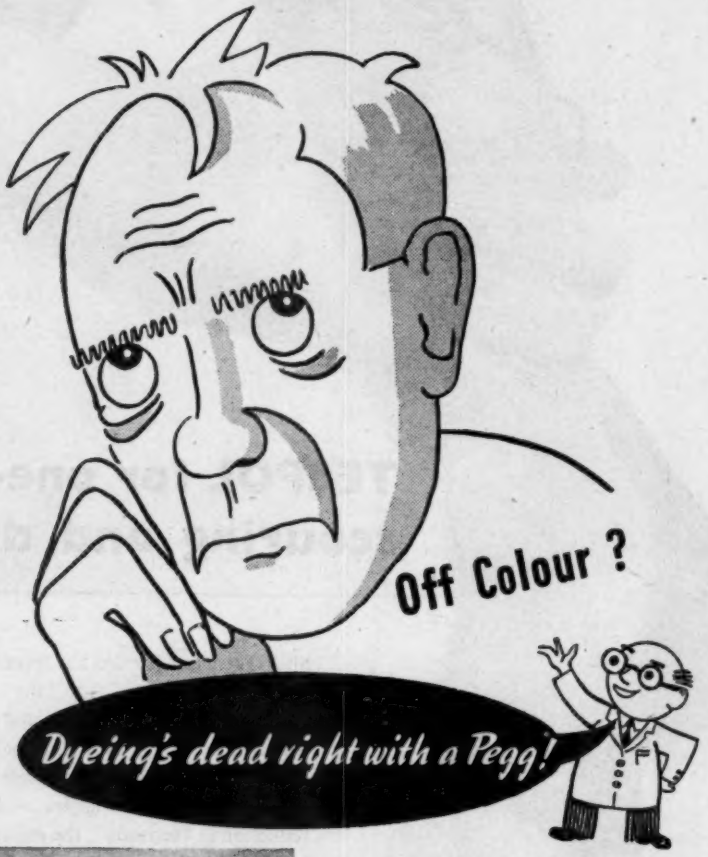

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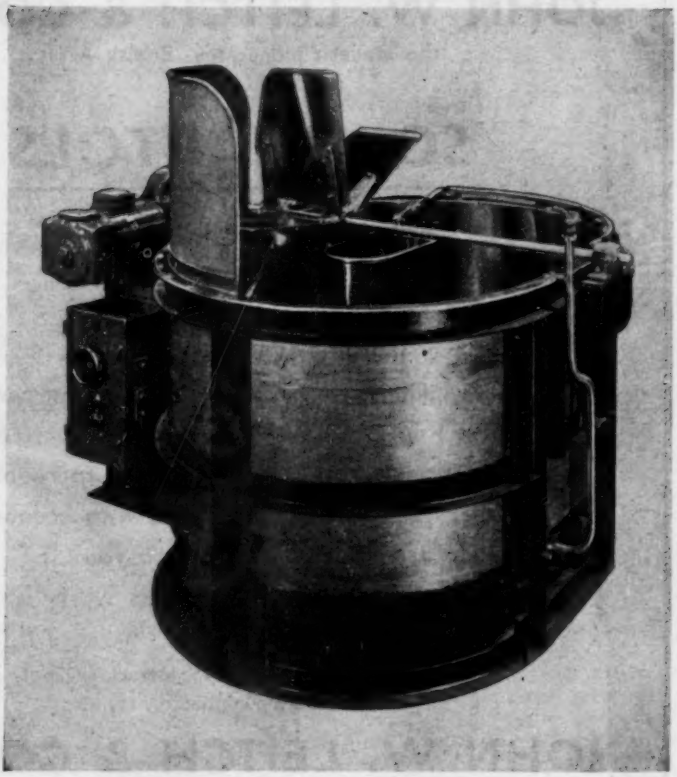

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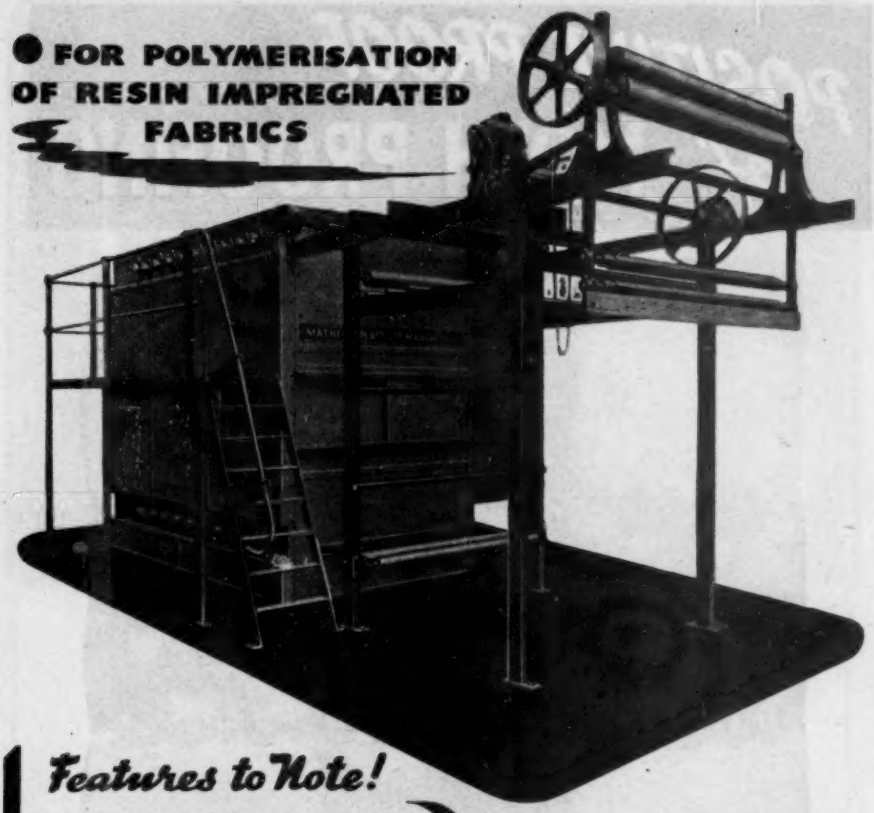

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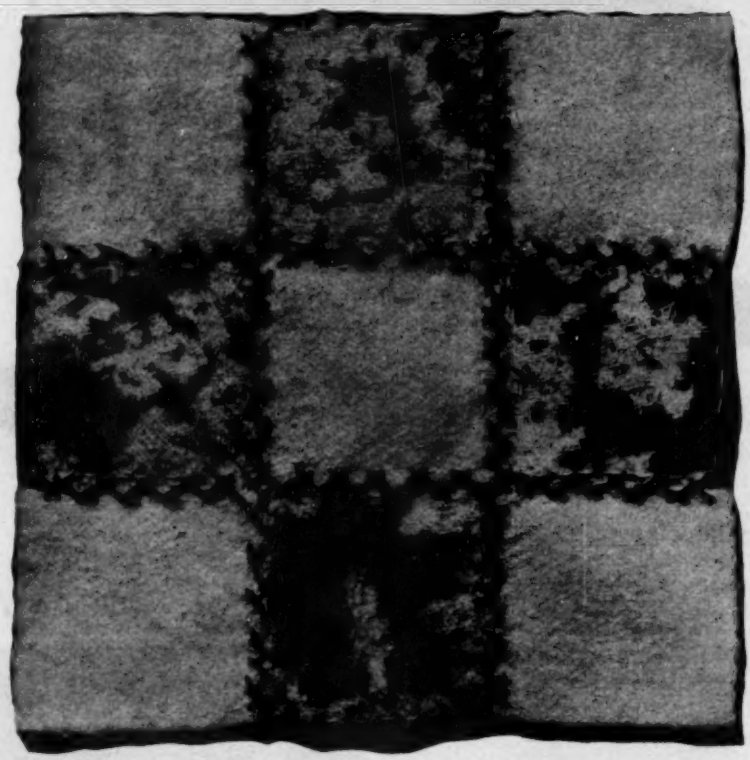

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NOTICE TO MEMBERS AND SUBSCRIBERS

Readers requiring *general information* regarding the Official Notices, List of Officers of the Society, etc. should consult pages 1–6 of the January 1951 and pages 345–348 of the July 1950 issues of the *Journal*, or write to *The General Secretary*, The Society of Dyers and Colourists, 32–34 Piccadilly, Bradford, Yorkshire (*Telephone* Bradford 25138–9). *Editorial Communications* should be addressed to *The Editor*, at the same address.

Forthcoming Papers

The following papers have been accepted by the Publications Committee, and will appear in future issues of the *Journal*—

COMMUNICATIONS

Some Observations on the Hardening Process used in Felt Manufacture. I— Factors influencing Hardening
R. S. M. Frohnsdorff and C. S. Whewell

Some Aspects of the Drying and Heating of Textiles—

IV— The Effect of Drying Conditions on the Latent Strain in the Yarn of Viscose Cakes
J. M. Preston and J. C. Chen

V— Migration in relation to Moisture Content
J. M. Preston and A. Bennett

Comparative Tests in Shrink-resisting Men's Half Hose
J. R. Stewart

Studies in the Fundamental Processes of Textile Printing. II— The Influence of Thickener Composition on Dye Transfer during Steaming
H. A. Turner and D. A. Reilly

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Forthcoming Meetings of the Society

1951

Friday 30th Mar. — ANNUAL GENERAL MEETING AND DINNER OF THE SOCIETY, GRAND HOTEL LEICESTER

Friday 20th April — EIGHTH MERCER LECTURE—Dr. D. Traill, St. Enoch Hotel, Glasgow

HUDDERSFIELD SECTION

All meetings held at Field's Cafe, Westgate, Huddersfield, at 7.30 p.m. unless otherwise stated

1951

Tuesday 27th Feb. — H. W. Ellis, Ph.D., A.R.C.S., A.R.I.C. *The Ellis Photometer*
F. L. Warburton, Esq. (W.I.R.A.) *Artificial Daylight Lamps*

Tuesday 20th Mar. — F. Jackson, Esq. *Water Treatment for Boilers and Processing*

Tuesday 10th April — ANNUAL GENERAL MEETING
Miss Esmee Smith. *Union Dyeing with Special Reference to Modern Fibres*

LONDON SECTION

All meetings held in the Rooms of the Royal Society, Burlington House, Piccadilly, London W.1, at 6 p.m. unless otherwise stated

1951

Friday 2nd Mar. — H. A. Turner, Esq. (Manchester College of Technology). *A Survey of the Results of Recent Research in Dyeing and Finishing.*

It is also intended to hold a Dinner and Dance in the New Year, and to arrange for a lecture to be given in Luton in the Spring, on a subject of interest to the hat industry.

MIDLANDS SECTION

All meetings commence at 7 p.m. (except where stated otherwise)

1951

Friday 23rd Feb. — MIDLANDS SECTION DINNER
King's Head Hotel, Loughborough

Wed. 21st Mar. 7.15 p.m. — *Recent developments in fluorescent lamps, with particular regard to colour problems.* Dr. S. T. Henderson (Joint meeting with British Association of Chemists). School of Arts and Crafts, Derby

Wednesday 18th April — ANNUAL GENERAL MEETING OF SECTION
King's Head Hotel, Loughborough

NORTHERN IRELAND SECTION

All meetings to be held in Queen's Hotel, Belfast, at 7.30 p.m.

1951

Wednesday 1st March — E. W. Goodale, Esq. (Warner & Son Ltd.) *Design in Furnishing Fabrics* (This will be a joint meeting with the Textile Institute)

March — Annual General Meeting and Dinner (Date to be announced later)

SCOTTISH SECTION

All meetings at 7 p.m. in St. Enoch's Hotel, Glasgow, unless otherwise stated

1951

Tuesday 20th Feb. — I. Gailey, B.Sc. *An investigation into the Unlevel Dyeing of Cotton Threads*

Tuesday 27th Feb. — G. L. Boardman, Esq. (Standfast Dyers and Printers Ltd.). *Developments in Continuous Dyeing.* (Joint meeting with the Textile Institute), School of Economics, Bell Street, Dundee. 7.30 p.m.

Tuesday 20th March — ANNUAL GENERAL MEETING. Followed by ordinary meeting at 7.30 p.m. Details to be announced later.

WEST RIDING SECTION

Meetings arranged for the Session 1950/1951
In Bradford, at the Great Northern Victoria Hotel, at 7.15 p.m.

1951

Thursday 22nd Feb. — Dr. R. L. Elliott (Bradford Technical College) *Modern Methods for the Investigation of Dyestuffs*

Thursday 8th Mar. — J. A. Potter, M.A. (C.A.C.). *Dyeing for the Hosiery Industry*

Thursday 15th Mar. — ANNUAL GENERAL MEETING

BRADFORD JUNIOR BRANCH

All meetings to be held in the Technical College, Bradford, at 7.15 p.m.

1951

Tuesday 27th Feb. — K. Richards, B.Sc., Dip.Ed. Lecture with film strip illustration, *The Scientific Story of Wool*

Monday 12th March — F. W. Bradley, Esq. (C.A.C. Ltd.). *The Application and Properties of Coprantine Dyes.* Lecture to be illustrated with many samples

Tuesday 20th March — STUDENTS' NIGHT

Monday 16th April — ANNUAL GENERAL MEETING

LEEDS JUNIOR BRANCH

All meetings to be held in the Colour Chemistry Lecture Theatre, Leeds University

1951

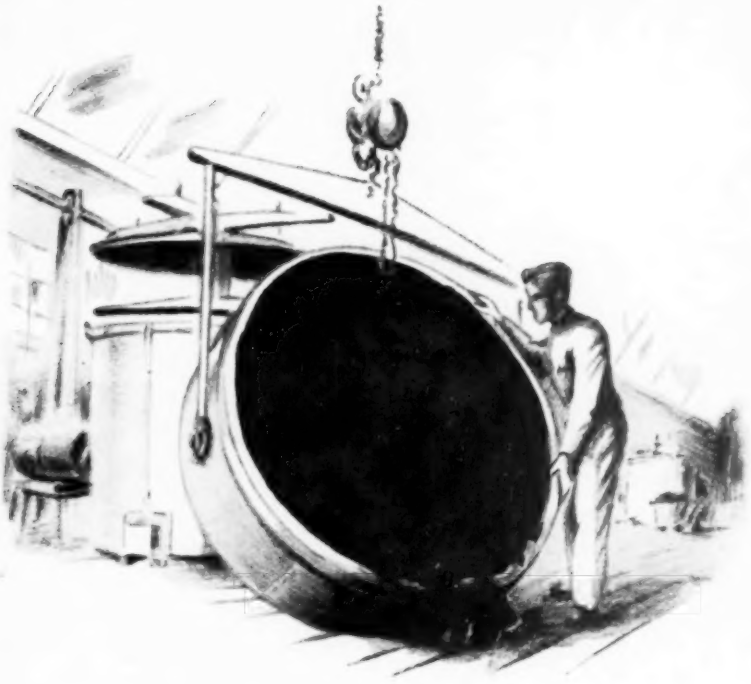
Tuesday 20th Feb. — Dr. T. Richardson (I.C.I. Ltd.). *Dyeing Practice Overseas.* 4 p.m.

MANCHESTER JUNIOR BRANCH

All meetings held in the Reynold's Hall, College of Technology, Manchester, at 6.30 p.m.

1951

Tuesday 3rd April — S. R. Cockett, M.Sc.(Tech.), F.R.I.C., of the Bradford Dyers' Association. *Detection and Correction of Faults in Dyed Materials*



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THE JOURNAL
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Volume 67—Number 2 FEBRUARY 1951 *Issued Monthly*

Proceedings of the Society

MIDLANDS SECTION

Meeting held at the King's Head Hotel, Loughborough, on 25th October 1950, Mr. W. L. LANGTON in the chair

Applications of the Report of the Committee on the Dyeing Properties of Wool Dyes

B. KRAMRISCH

It is not possible to be dogmatic as to what is the most important property of a dye, but it will no doubt be generally accepted that the dyeing and levelling properties merit primary consideration. After all, the first point to be considered by the purchaser of dyed materials is levelness of shade, and it is well known that an intimate knowledge of the dyeing properties of individual dyes is essential in deciding on their usefulness and method of application.

The *Report of the Committee on the Dyeing Properties of Wool Dyes*[1] (subsequently called the *Report* in this paper) includes suggested methods of standardizing the dyeing and migrating properties of both molecularly dispersed and aggregated wool dyes. Chrome and premetallized dyes are not included, but nevertheless the types of dyes investigated cover a wide field.

The first part of the Report, on the standardization of methods of determining optimum dyeing properties, calls for little additional comment, as its principal object was to rationalize the various methods adopted by dyemakers in grouping their products.

The second part of the Report, dealing with a standard method of assessing the migrating properties of wool dyes, is of fundamental importance. Even if the initial strike of a dye is not too satisfactory with respect to levelling, then provided the dye exhibits good migrating properties, this initial defect will be overcome, to a greater or less degree, during the progress of the dyeing operation. The migrating properties are also of importance when shading to pattern, as normally the period of dyeing here is shorter than that employed during the initial part of the process.

Strike is an important factor, especially during the initial period whilst the dyebath is being raised to the boil, and although a standard method of determining strike was not included in the Report, it was felt that the dyeing test would provide some information in this connection.

As the proposed tests were confined to molecularly dispersed and aggregated acid dyes on wool, they will apply mainly to the dyeing of yarns, piece goods, fabric, felts, hoods, and hose, and to a much lesser extent to loose wool and slubbing. They thus cover the dyeing of all types of materials in open pans or paddle machines; loose wool in liquor-circulating machines; slubbing in cans and Hussong and Klauder–Weldon machines; yarns in the latter two machines, and also in Pegg Pulsator and Freeman–Taylor Plusflo machines; woven piece goods, flat felts, and knitted fabric in open or enclosed winches; and hose and hoods in the usual types of machines.

As the Report deals solely with wool dyes on normally scoured wool, it is of interest to see how far the proposed tests are applicable in other directions.

NON-SHRINK WOOL

Wool dyes are used on wool which has been subjected to various chemical pretreatments, such as carbonizing or bleaching by peroxide or sulphur stoving, which in several instances modify its dyeing behaviour. The most important such process to-day, however, is some form of non-shrink treatment. This type of treatment really came into its own during the war, and has since spread to many branches of the civilian trade, especially for half-hose, knitting yarns, and underwear.

It is well known that some non-shrink treatments can affect the levelling and rate of strike of a dye as well as its wet-fastness properties, but only levelling is to be considered here. In order to investigate this point, lengths of botany serge, prepared and scoured ready for dyeing, were

treated in bulk by six representative non-shrink processes operated in this country. The migrating properties of a number of dyes were then compared on the six different non-shrink wools and also on untreated wool, the results obtained being given in Table I. In carrying out these tests by the prescribed method, the exhaustion of the dyebaths was estimated by means of a Microptic Duboscq-type colorimeter (Hilger & Watts) and the pH with a glass-electrode pH meter (Muirhead).

Both dyeing and migration tests were carried out in 500-ml. conical flasks fitted with finger condensers in thermostatically controlled, electrically heated stainless steel dyebaths (Laboratory Thermal Equipment Ltd., Greenfield, near Oldham) using glycerol (technical) at 120°C.

Loose materials and slubbing were placed inside bags made of unbleached cotton cheese cloth.

The migration figures were assessed by means of S.D.C. Grey Scale No. 2.

TABLE I

Migration Test on Non-shrink Wools

Dye	0·4% Orange II	0·85% Brilliant Scarlet R	1·3% Alizarine Fast Blue 2BG	0·9% Cloth Fast Orange 2R	0·9% Cloth Fast Red GR	1·4% Cloth Fast Brilliant Blue R
Colour Index No.	151	—	—	—	430	—
Dyeing Method	I	III	III	IV	IV	IV
Non-shrink Treatment			Migration			
None	5	3	2	1	1	1
Permanganate and hypochlorite	5	2	2	1	1	1
Alkali and organic solvents	5	4–5	2–3	1	1	3
Peroxide and metal salts	5	4	3	1–2	1	2
Wet chlorination	5	3–4	2	1	1	2
Enzyme	5	2	2	1	1	1–2
Dry chlorination	5	3–4	2–3	1	1	2

The following conclusions can be drawn from these results—

(1) A dye of excellent migrating properties, Orange II, gives equally good results on all the types of wools examined.

(2) Brilliant Scarlet R, a dye showing average migration on untreated wool, exhibits increased migration on wool treated with alkali and organic solvents or with peroxide and metal salts, and slightly decreased migration on wool treated with permanganate and hypochlorite or with enzymes. Table II indicates the interesting property of decreased exhaustion after the permanganate–hypochlorite and peroxide–metal salts treatments.

(3) Whilst noticeably increased migration is shown with Cloth Fast Brilliant Blue R after both alkali and peroxide treatments and both chlorination processes, there is no appreciable difference with the other two Cloth Fast dyes examined, all three showing a low migration figure on untreated wool.

TABLE II

Exhaustion of 0·85% Brilliant Scarlet R with Non-shrink Wools

(Dyed by Method III)

Non-shrink Treatment	Exhaustion of Dyebath (%)	Final pH of Dyebath
None	89·9	4·7
Permanganate and hypochlorite	84·5	4·2
Alkali and organic solvents	90·0	4·7
Peroxide and metal salts	77·5	4·5
Wet chlorination	92·0	4·0
Enzyme	93·5	4·1
Dry chlorination	90·5	4·35

HAIRS

After wool had been dealt with, the next logical step appeared to apply the tests to hairs. These are protein fibres bearing a close chemical relationship to wool, but showing some differences in fibre structure and physical characteristics.

Fibres of this type include alpaca, angora, camel hair, cashmere, and mohair. Alpaca and mohair are mainly top-dyed, although some is piece-dyed for linings. Mohair may also be dyed as yarn and in the form of pile fabric, and in addition is sometimes mixed with wool for tropicals and piece-dyed. Camel hair and cashmere are usually dyed in the loose state or in top form, whilst angora is yarn-dyed. Cow hair and bull's wool also fall into this category, and are usually mixed with wool in the manufacture of certain types of flat felts. Horse hair, pigs' bristles, badger hair, etc. are also included in this class, but are dyed only in special instances.

Migration tests were carried out on four of the principal fibres in this group with three representative dyes, the results being compared with those for wool (Table III).

TABLE III

Migration Tests on Hairs

Dye	0·4% Orange II	0·85% Brilliant Scarlet R	1·4% Cloth Fast Brilliant Blue R
Colour Index No.	151	—	—
Dyeing method	I	III	IV
Material		Migration	
Wool	5	3	1
Alpaca (top)	4–5	3	1
Camel (top)	5	3	1
Cashmere (loose)	5	4	2
Mohair (yarn)	4	3	1

As will be seen, cashmere tends to show improved migration compared with wool and the other fibres. This behaviour may link up with the fact that most wool dyes show inferior wet fastness, such as fastness to washing, on cashmere compared with wool.

FURS

Rabbit and to a lesser extent hare fur are the main fibres of this group to be taken into consideration, and although they bear a close relationship to wool and hairs in many respects, they differ fundamentally in scale structure. Before they can be used in hat manufacture, furs have to be carrotted, i.e. treated by various chemical processes in order to improve their felting properties. Up

till fairly recent times some form of mercuric carrotting was used, but this is now being replaced to an appreciable extent by non-mercuric processes, which offer certain advantages, particularly in view of the possible toxic effect of mercury compounds on the operative.

Tests carried out on mercuric and non-mercuric carrotted rabbit fur and on wool showed similar migration values for all three fibres (Table IV).

TABLE IV

Migration Tests on Furs

Dye	0·4% Orange II	0·85% Brilliant Scarlet R	1·4% Cloth Fast Brilliant Blue R
Colour Index No. ...	151	—	—
Dyeing method ...	I	III	IV
Material		Migration	
Wool	5	3	1
Mercuric carrotted fur	5	3	1
Non-mercuric carrotted fur	5	3	1

SILK

Silk differs fundamentally in morphological structure and physical characteristics from wool, hairs, and furs. It does, however, bear some chemical relationship to these fibres, the chief difference being the absence of sulphur in silk. Comparative migration tests were carried out on wool and silk with three dyes, and somewhat lower migration figures were obtained in each case with silk than with wool (Table V).

TABLE V

Migration Tests on Silk

Dye	0·35% Citronine OOO	1·7% Benzyl Green B	1·0% Benzyl Fast Blue 3GL
Colour Index No.	145	667	—
Dyeing method	I	I	III
Material		Migration	
Wool	3–4	3	3–4
Silk (piece) ...	3	2	3

REGENERATED PROTEIN FIBRES

Owing to economic factors and certain characteristic properties, there is a tendency to blend a proportion of regenerated protein fibres with wool. Migration tests were carried out with three dyes on wool, loose Ardil, and Lanital yarn.

From Table VI it will be seen that the three dyes examined tended to give lower migration on Ardil than on wool*, and slightly greater migration on Lanital than on the latter material. It will be noticed that in this series of tests Orange II has been dyed by method II in place of method I, as an organic acid is preferable to a mineral acid to preserve more fully the condition of regenerated protein fibres.

TABLE VI

Migration Tests on Regenerated Protein Fibres

Dye	0·4% Orange II	0·85% Brilliant Scarlet R	1·4% Cloth Fast Brilliant Blue R
Colour Index No.	151	—	—
Dyeing method...	II	III	IV
Material		Migration	
Wool	5	3	1
Ardil	4	1	1
Lanital	5	3–4	2

MISCELLANEOUS MATERIALS

Some consideration should also be given to the application of wool dyes to materials other than those already discussed.

Appreciable quantities of wool dyes are used on leather and to a lesser extent on sheepskins, both of these materials being related chemically to wool. Leather and sheepskins, however, are dyed at temperatures well below the boil, and consequently the proposed dyeing and migration tests do not apply. Wool dyes are also used for non-protein materials, for example in the dyeing of anodized aluminium and in the staining of crêpe paper. The dyeing technique for the latter materials is, however, so different from that employed in wool dyeing that the application of the proposed tests can be ruled out of consideration.

NYLON

Another non-protein fibre, nylon, can however be dyed with wool dyes selected from the groups covered in the Report, using the normal methods, so that tests have been carried out on this fibre.

Migration tests were carried out with several dyes on filament nylon piece (parachute cloth) and spun nylon yarn, the results being compared with those for wool (Table VII).

It will be seen that the degree of migration is noticeably lower with nylon than with wool, and

* This is due to the acid content of Ardil (pH of aqueous extract = 2·4). If Ardil is neutralized, the migration is equal to or better than that on wool.

TABLE VII

Migration Tests on Nylon

Dye	0·4% Orange II	0·35% Citronine OOO	1·3% Alizarine Sapphire Blue CB	1·5% Alizarine Sapphire Blue CR	0·85% Brilliant Scarlet R	2·6% Alizarine Fast Rubine 4B	1·3% Alizarine Fast Green G	1·1% Cloth Fast Brilliant Blue G	1·4% Cloth Fast Brilliant Blue R	0·6% Cloth Fast Green B
Colour Index No.	151	145	1054	1076	—	—	1078	—	—	—
Dyeing method	I	I	I	I	III	III	III	IV	IV	IV
Material						Migration				
Wool	5	3–4	3–4	3–4	3	3	2	1	1	2
Filament nylon	3	2	2	2	1	2	1	1	1	1
Spun nylon ...	3	2	2	2	2	1–2	1	1	1	1

that filament and spun nylon behave in a fairly similar manner in this regard.

It is known that structural irregularities in nylon fibre can occur during the drawing process in the course of manufacture, and these can affect its dyeing properties, giving "barry" dyeings.

Similar teething troubles were encountered in the early days of the manufacture of filament viscose rayon. These difficulties, however, have now been overcome to an appreciable extent, and no doubt similar success will be achieved with nylon in the near future.

The most level results on so-called "barry" nylon, especially woven and knitted material and hose, are normally obtained with dispersed acetate rayon dyes, and dyeings obtained with water-soluble dyes are not as satisfactory in this respect. No doubt the lower migration of wool dyes on nylon as compared with wool will to some extent account for these difficulties.

It should not be overlooked that the tests described above have been carried out at concentrations which should be below the saturation values for the dyes in question on nylon, and if the saturation values are exceeded, anomalous results may be observed.

CONTINUOUS DYEING PROCESSES

It has been assumed in this paper that the methods of testing in the Report would be applicable to established methods of wool dyeing to cover current industrial practice for wool in the loose state or in the form of slubbing, yarn, hose, hoods, fabric, flat felt, or piece goods, all of which are batch or non-continuous processes. Experimental evidence has then been presented to show that the tests in question give useful information on the behaviour of wool dyes on other materials such as hairs, fur, silk, regenerated protein fibres, and nylon.

With regard to the future, it must be appreciated that several revolutionary ideas have been suggested for dyeing wool, the general trend, in contrast to present practice, being to develop continuous processes. At the moment, apart from isolated cases such as the dyeing of loose wool with indigo in the Petrie and McNaught scouring machine, the continuous dyeing of wool is virtually non-existent in commercial practice, at any rate in Britain.

Casty and Krähenbühl[2] have proposed a continuous or "sudden contact" method for wool dyeing, which is now embodied in a patent specification[3]. Robinson and Zimmerman[4] suggest dyeing wool continuously at 275°F., and claim that the Uxbridge high-temperature continuous-dyeing machine permits the dyeing of wool at 25 yards per minute. The Standfast molten metal dyeing process[5], although primarily designed for the application of vat dyes to cotton, also includes wool in the patent specification[6]. A continuous process for surface-active wool dyes which normally do not level too well has also been patented[7].

As it is quite possible that processes of this type will come into commercial operation in the future, it is necessary to review the Report and also this paper with this possibility in mind. The new principles involved, which in many cases differ fundamentally from present industrial practice, will no doubt limit the application of the tests in question, and the proposed new techniques will therefore present problems for a future committee to investigate.

I acknowledge my indebtedness to the Clayton Aniline Co. Ltd. for permission to publish this paper and to Mr. D. G. Evans for his assistance with the practical work involved.

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Discussion

Mr. S. SHAW: Has the Lecturer taken into account the degree of sulphonation of the acid dyes which have been compared for migration properties on wool and nylon?

Mr. KRAMRISCH: No. I merely selected several dyes which were suitable for dyeing both wool and nylon.

Mr. A. W. CARPENTER: Do the dyemakers intend to incorporate the new tests in their pattern cards, and further will the Society include them in the new *Colour Index*?

Mr. KRAMRISCH: My firm is using the tests for comparing different dyes, and eventually hopes to have available the results of the new migration test on its molecularly dispersed and aggregated wool dyes.

Mr. D. HAIGH: At the recent Summer School in Leeds, the tests in question were demonstrated to a large number of students, who were all able to reproduce the expected results.

It is unfortunate that no strike test is given in the Report.

Dr. P. W. CUNLIFFE: Although it is too late now to include the assessment of dyes by the proposed tests in the new *Colour Index*, no doubt this will be practicable at a later date if and when revision takes place.

The Wool Dyes Committee spent considerable time in trying to work out a suitable strike test, but was not successful.

Mr. A. W. CARPENTER: In the Midlands, yarn and footwear are dyed in certain instances by entering the material at the boil, and it is sometimes found with certain dyes, such as the Fast Light Yellow 2G type, that the expected level results are not obtained. Has the Committee considered this point?

Mr. KRAMRISCH: The proposed tests do not cover the question of entering the material at the boil. We have not been able to allow for all contingencies, and tests have had to be evolved

which would cover the bulk of current trade practice. For this reason the dyeings and tests were all commenced at a relatively low temperature.

Further, in the initial work, the migration test was for 30 min. only, but as anomalous results were encountered, in particular with dyes of the type mentioned by Mr. Carpenter, the migration test was extended to 1 hr., and the results then obtained fitted in better with bulk experience.

Mr. S. Shaw: What is the relative washing fastness of acid wool dyes on nylon and wool? Also, has the Committee considered applying the same dye on wool and nylon by different methods?

Mr. Kramrisch: If a wool dye exhibits satisfactory affinity for nylon, the wet fastness properties, including fastness to washing, are on the whole at least equal to, and normally better than, those of the corresponding dye on wool at the same depth.

With regard to the second question, although certain wool dyes are normally applied to nylon with acetic acid in preference to sulphuric acid, for the purpose of these tests it is considered preferable to use the same dyeing method for the two fibres with each dye.

Mr. W. A. Edwards: As I am particularly interested in nylon-spliced footwear requiring the use of chrome dyes, I have not used the tests in question, since they are limited to the acid levelling and milling types of dyes. On the other hand, for certain trades which require the use of dyes to meet increased wet-fastness requirements, the tests should be of value in assessing the compatibility of dyes for use in combination shades.

Mr. Kramrisch: Although quite a fair amount of work was carried out by the Committee with chrome dyes, considerable difficulties were encountered with this group, and the work was abandoned.

COMMUNICATIONS

Combination of Wool with Acids in presence of Salts

Bertil Olofsson

1. Titrations of wool with hydrochloric acid in the presence of sodium chloride, sodium sulphate, potassium chloride, potassium sulphate, and barium chloride, and with sulphuric acid in the presence of sodium chloride and sodium sulphate, have been performed, the absorption of hydrogen, chloride, and sulphate ions being determined.

2. The presence of sulphate ions always gives greater absorption of hydrogen ions than does that of chloride ions.

3. A critical review of absorption theories is given, as regards their value for interpreting the experimental results.

4. Both the Gilbert–Rideal and the Donnan theories are used for accurate comparison with the experiments; the former gives quite satisfactory results, but the latter gives only qualitative agreement.

5. It is concluded that chloride and sulphate ions are not dispersed at random in the fibre phase, but are to some extent localized at positive sites, the former having greater affinity for the wool fibre than the latter ions.

INTRODUCTION

Titration with acids was early recognized as a valuable method of investigating the internal structure of wool. The first accurate titration curves for certain acids were determined by Speakman and Hirst[1] and by Speakman and Stott[2]. Extensive experimental studies have later been carried out by Steinhardt and co-workers[3–7], who also studied the influence of salts containing the same anion as the acid. Some careful titrations have also been performed by La Fleur[8].

It seemed of interest to investigate the effect on the acid-binding capacity of ions different from those of the acid present. The experimental results would probably not be the same if the equilibrium between absorbed ions and ions in solution is a Donnan equilibrium as if the ions have some affinity for the wool keratin. As differences were actually found, a more careful study of the binding of hydrochloric acid in the presence of sodium sulphate and of sulphuric acid in the presence of sodium chloride was made, the amounts absorbed of all the ions present being determined.

SYMBOLS

The following symbols are employed—

A_X = Quantity of X absorbed in millimoles per gram of dry wool

$\theta_X = \dfrac{A_X}{A_{X\,max}}$

$\theta' = \dfrac{\text{Number of COOH groups on fibre}}{\text{Number of COOH} + \text{COO}^- \text{ groups on fibre}}$

c_X or $[X]$ = Concentration of X in gram-molecules per litre

a_X or (X) = Activity of X

f_X = Activity coefficient of X

μ_X = Chemical potential of X

μ_X° = Chemical potential of X in standard state (at given pressure and temperature)

V = Electrostatic potential of fibre

z = Ionic valency

F = Faraday

R = Molar gas constant

T = Absolute temperature

λ = Donnan quotient = $e^{VF/RT}$

v = Volume of internal solution per gram of dry wool

EXPERIMENTAL

Titrations with hydrochloric acid were made in parallel experiments in the presence of 0·1 *N.* solutions of (*a*) sodium chloride, (*b*) sodium sulphate, (*c*) potassium chloride, (*d*) potassium sulphate, and (*e*) barium chloride.

The wool used was a 58s South American crossbred. The samples were first extracted with ether,

then washed for a long time in distilled water, and finally dried at 50°c. The solutions (60 ml.) were prepared from 0·2 N. salt solutions and 0·1 N. hydrochloric acid. The wool samples (1 g.) were placed in the solutions in glass- or rubber-stoppered bottles. The bottles were occasionally swirled. After at least 48 hr. the first titrations were made. By means of a calibrated pipette 10 ml. of the solution was removed and titrated with 0·1 N. caustic soda. A second 10 ml. was taken for potentiometric pH determination. This liquid was afterwards replaced by 10 ml. of 0·2 N. salt solution, an arbitrary volume (n ml.) of 0·1 N. hydrochloric acid, and $10 - n$ ml. of water. The volume n was chosen so as to give a greater (or smaller) concentration of acid in the bath than was found from the titration. The samples were left for at least a further 48 hr., when they were titrated, the pH was again measured, and more acid was added. In this manner a great part of the titration curve was determined. Another part could be determined by using new samples and a definitely greater (or smaller) amount of acid from the beginning. Finally, the wool samples were dried and accurately weighed.

The same kinds of titrations were made with sulphuric acid in parallel experiments in the presence of (*a*) sulphuric acid alone, (*b*) 0·1 N. sodium chloride, and (*c*) 0·1 N. sodium sulphate.

Finally, determinations of all the ions absorbed were made with hydrochloric acid–sodium sulphate and sulphuric acid–sodium chloride solutions. 70-ml. solutions were prepared from 35 ml. of 0·2 N. sodium sulphate or chloride, n ml. of 0·1 N. hydrochloric or sulphuric acid respectively, and $(35 - n)$ ml. of water, 1-g. wool samples being used. After 48 hr. the composition of the bath was determined: 10 ml. was titrated with caustic soda, 10 ml. used for pH determination, 10 ml. titrated for chloride by the Volhard method[98], and 10 ml. used for sulphate determination by the ordinary gravimetric method of precipitation with barium chloride[99]. To get good accuracy microburettes were used for measuring the volumes of liquid in these determinations.

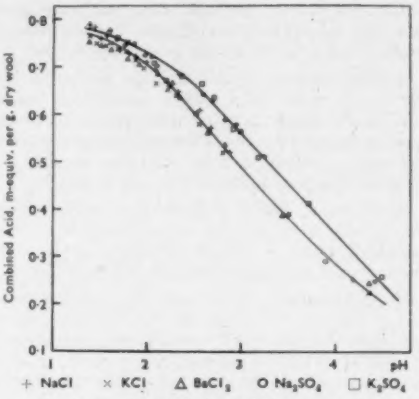

FIG. 1— Titration of Wool with Hydrochloric Acid in presence of 0·1 N. Salt

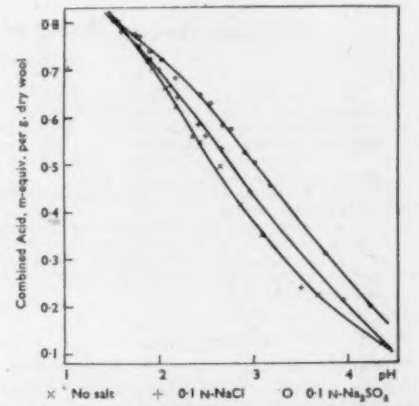

FIG. 2— Titration of Wool with Sulphuric Acid in Presence and Absence of Salt

RESULTS

The quantities of acid absorbed in the titrations with successively increased acid concentration were calculated from the titration results and the amounts of acid added to replace the liquid removed.

If the normality of the acid differs from 0·1, the corresponding correction should, of course, be made, and corrections for calibrated volumes of pipettes must also be made. The absorbed quantities were calculated as millimoles of hydrogen per gram of dry wool. The measured pH values were sometimes compared with the measured concentrations. The activity coefficients f_{H^+} were calculated from the equation—

$$-\log f_{H^+} = pH + \log c_{H^+}$$

and always found to be in reasonable agreement with the theoretical values. The absorption A_{H^+} was plotted against the measured pH (Fig. 1). The titrations with sulphuric acid were made in the same manner as those with hydrochloric acid and the same calculations were performed (Fig. 2).

Accurate determinations of hydrogen, chloride, and sulphate ion concentrations were made on six samples of hydrochloric acid–0·1 N. sodium sulphate and six samples of sulphuric acid–0·1 N. sodium chloride, and here every sample was used for only one experiment.

The amount absorbed A was calculated as before as the difference between the total amount added and the amount found from titration, the volume of the solution (70 ml.) being assumed to be the same before and after equilibrium was attained. The results are given in Tables I and II.

DISCUSSION OF RESULTS

The titration curves with hydrochloric acid (Fig. 1) show no great variation when different salts are present. However, the plots for the three chlorides seem to give one curve, while those for the two sulphates give another. Within these two

TABLE I

Titration with 0·1091 N-HCl + 0·0988 N-Na_2SO_4

Sample	Dry Weight of Wool (g.)	Acid added (ml.)	pH	c_H	A_H	c_{Cl}	A_{Cl}	c_{SO_4}	A_{SO_4}
1	0·8941	2·00	4·44	2×10^{-4}	0·225	$1·7 \times 10^{-3}$	0·056	0·0483	0·085
2	0·8949	4·00	3·52	9×10^{-4}	0·420	$4·0 \times 10^{-3}$	0·083	0·0473	0·168
3	0·8933	6·00	2·99	$2·5 \times 10^{-3}$	0·539	$7·2 \times 10^{-3}$	0·095	0·0466	0·222
4	0·8923	10·00	2·46	$7·4 \times 10^{-3}$	0·643	$1·25 \times 10^{-2}$	0·098	0·0459	0·273
5	0·8949	20·00	1·93	$2·11 \times 10^{-2}$	0·787	$2·68 \times 10^{-2}$	0·163	0·0454	0·313
6	0·8928	35·00	1·57	$4·37 \times 10^{-2}$	0·853	$4·88 \times 10^{-2}$	0·301	0·0459	0·276

TABLE II

Titration with 0·1024 N-H_2SO_4 + 0·1000 N-NaCl

Sample	Dry Weight of Wool (g.)	Acid added (ml.)	pH	c_H	A_H	c_{Cl}	A_{Cl}	c_{SO_4}	A_{SO_4}
1	0·8696	2·00	4·62	1×10^{-4}	0·226	0·0949	0·266	$1·7 \times 10^{-3}$	−0·020
2	0·8908	4·00	3·48	7×10^{-4}	0·404	0·0967	0·426	$3·1 \times 10^{-3}$	−0·011
3	0·8907	6·00	2·98	$2·0 \times 10^{-3}$	0·533	0·0911	0·454	$3·3 \times 10^{-3}$	0·039
4	0·8928	10·00	2·28	$6·6 \times 10^{-3}$	0·630	0·0917	0·497	$6·5 \times 10^{-3}$	0·066
5	0·8912	20·00	1·92	$2·06 \times 10^{-2}$	0·684	0·0907	0·372	$1·26 \times 10^{-2}$	0·156
6	0·8936	35·00	1·62	$4·12 \times 10^{-2}$	0·787	0·0918	0·306	$2·25 \times 10^{-2}$	0·240

groups no real differences can be detected. Thus the difference appears to be associated with different effects of the negative ions, Cl^- and SO_4^{2-}, the latter giving the greater absorption. As regards the titrations with sulphuric acid (Fig. 2), a corresponding difference is obtained between sodium chloride and sulphate, the latter salt again giving the greater absorption.

It has been suggested that a considerable exchange of ions occurs, i.e. that in reality the titration is performed not with hydrochloric or sulphuric acid but with a mixture of hydrogen, chloride, and sulphate ions. Thus the experiments including accurate determinations of all ions present had to be performed. Tables I and II show that the assumption of ion exchange is justified.

It should be possible to compare the figures obtained with those predicted by theory, based on the assumption of the presence of free carboxyl and amino groups in wool. These groups are mainly the free parts of the dicarboxylic and diamino acids linked in the peptide chains. There are about the same number of acid as basic groups, and as these groups are in appropriate positions, salt linkages are established between them—

$$-COOH + NH_2- \rightarrow -COO^-[NH_3^+]-$$

Thus titration with acid should be of the type—

$$-COO^- + HA \rightarrow -COOH + A^-$$

The total amount of acid combined, however, corresponds to the total amount of amino groups, as possibly not all of these groups are salt-linked.

The theory of acid binding has been considered by Speakman and Hirst[1], Elöd and Silva[10], Steinhardt, Fugitt, and Harris[3,5], La Fleur[11], Gilbert and Rideal[12], and Peters and Speakman[13]. The work of Speakman and Hirst and of Elöd and Silva is founded on Procter and Wilson's[14] use of the Donnan equilibrium in explaining the protein–acid behaviour, and Peters and Speakman's latest work is an accurate interpretation from the Donnan theory. La Fleur draws a theoretical titration curve by adding the titration curves for the single amino acids, constructed from the dissociation constants of their active amino and carboxyl groups and the relative amounts of these acids in wool. He makes a correction for the position of the amino acids in polypeptides, but these curves are not in good agreement with the experimental curves, probably because there is no real consideration of the unique liquid–solid phase equilibrium. Steinhardt *et al.* take the possibility of anion affinity for wool into consideration and describe the acid–wool behaviour in terms of association reactions between isoelectric wool $W^{\pm}$ and acid ions H^+ and A^-, giving the protolytic products WH^+, WA^-, and WHA. However, their theoretical results are not in good agreement with experiment, and the theory has been criticized from different points of view[12,13].

An attempt has been made to calculate, by the method of Steinhardt *et al.*[3], the ionization constants for the binding of pure hydrochloric acid from the experimental results in the present paper. The fraction θ is given by—

$$\theta = \frac{A_{H^+}}{A_{H^+\,max}} = \frac{[WHCl] + [WH^+]}{[WHCl] + [WH^+] + [W^{\pm}]} \qquad \text{(i)}$$

and this expression is transformed to—

$$\theta = \frac{1}{1 + \dfrac{K_H K_{Cl}}{[H^+](K_{Cl} + [Cl^-])}} \qquad \text{(ii)}$$

where

$$K_H = \frac{[W^{\pm}]\,[H^+]}{[WH^+]} \qquad \text{(iia)}$$

and

$$K_{Cl} = \frac{[WH^+]\,[Cl^-]}{[WHCl]} \qquad \text{(iib)}$$

Equation (ii) is then rearranged (assuming $[H^+] = [Cl^-]$) to give—

$$\frac{1}{[H^+]\left(\frac{1}{\theta} - 1\right)} = \frac{1}{K_H} + \frac{[H^+]}{K_H K_{Cl}} \qquad \text{(iii)}$$

Thus the experimental values of $1/[H^+](1/\theta - 1)$ plotted against $[H^+]$ should give a straight line,

from which the constants K_H and K_{Cl} could be determined. But the resulting graph is highly curved, and the constants cannot be determined by extrapolation. To some extent this result contradicts Peters and Speakman's calculation of dissociation constants[12], but these authors have used expression (i) with [WCl⁻] included in the denominator, following Steinhardt and Harris[3]. However, they have pointed out the poor agreement between constants derived from experimental curves and those based on the theoretical conclusions of Steinhardt *et al.*

Thus the present results remain to be compared with the Gilbert–Rideal theory and with the Donnan theory.

THE GILBERT–RIDEAL INTERPRETATION

We assume that chemical equilibrium is established between ions X in solution, where the chemical potential has the ordinary form—

$$\mu_X = \mu_X^\circ \text{ (soln.)} + RT \ln a_X \qquad \text{(iv)}$$

and ions absorbed on fibre sites, where the potential calculated from statistical thermodynamics should be—

$$\mu_X = \mu_X^\circ \text{ (fibre)} + RT \ln \frac{\theta_X}{1 - \Sigma\theta_X} + z_X VF \qquad \text{(v)}$$

Here $\Sigma\theta_X$ means the relative amount absorbed of all ions of the same sign as the ion X. By equating (iv) and (v) we get—

$$RT \ln \frac{\theta_X}{1 - \Sigma\theta_X} = -(\mu_X^\circ \text{ (fibre)} - \mu_X^\circ \text{ (soln.)}) + RT \ln a_X - z_X VF \qquad \text{(vi)}$$

Thus

$$\log \frac{\theta_X}{1 - \Sigma\theta_X} = -\frac{\Delta\mu_X}{RT} \log e + \log a_X - \frac{z_X VF}{RT} \log e \qquad \text{(via)}$$

where $\Delta\mu_X$ is constant for each ion, giving a measure of its affinity for the fibre.

If we apply (via) to the three different ions H^+, Cl^-, and SO_4^{2-} we get the equations—

$$\log \frac{\theta_H}{1 - \theta_H} = -\text{pH} - \frac{\log e}{RT}(\Delta\mu_H + VF) \qquad \text{(vii)}$$

$$\log \frac{\theta_{Cl}}{1 - \theta_{Cl} - \theta_{SO_4}} = \log a_{Cl} - \frac{\log e}{RT}(\Delta\mu_{Cl} - VF) \qquad \text{(viii)}$$

$$\log \frac{\theta_{SO_4}}{1 - \theta_{Cl} - \theta_{SO_4}} = \log a_{SO_4} - \frac{\log e}{RT}(\Delta\mu_{SO_4} - 2VF) \qquad \text{(ix)}$$

We may eliminate the terms in V between (vii) and (viii) and between (vii) and ix)—

$$\log \frac{\theta_H}{1 - \theta_H} + \log \frac{\theta_{Cl}}{1 - \theta_{Cl} - \theta_{SO_4}} = -\frac{\log e}{RT}(\Delta\mu_H + \Delta\mu_{Cl}) - \text{pH} + \log a_{Cl} \qquad \text{(x)}$$

$$2 \log \frac{\theta_H}{1 - \theta_H} + \log \frac{\theta_{SO_4}}{1 - \theta_{Cl} - \theta_{SO_4}} = -\frac{\log e}{RT}(2\Delta\mu_H + \Delta\mu_{SO_4}) - 2\,\text{pH} + \log a_{SO_4} \qquad \text{(xi)}$$

Further, the condition of electrical neutrality of the fibre is—

$$\theta_H = 2\theta_{SO_4} + \theta_{Cl} \qquad \text{(xii)}$$

as the bivalent SO_4^{2-} ion should occupy only one negative site[13]. From (x), (xi), and (xii) the quantities θ_H, θ_{Cl}, and θ_{SO_4} may be calculated if the $\Delta\mu_X$ terms and the ionic activities in solution are known.

The $\Delta\mu_X$ values were calculated from titration curves of the pure acids. For pure hydrochloric acid we put $\theta_{SO_4} = 0$, giving from (xii) $\theta_H = \theta_{Cl}$; and if $f_H = f_{Cl}$, then $\text{pH} = -\log a_{Cl}$, and we get from (x)—

$$\log \frac{\theta_H}{1 - \theta_H} + \text{pH} = -\frac{\log e}{2RT}(\Delta\mu_H + \Delta\mu_{Cl}) \qquad \text{(xiii)}$$

For pure sulphuric acid we put $\theta_{Cl} = 0$, giving $\theta_H = 2\theta_{SO_4}$; and as $f_H = f_{SO_4} \simeq 1$ for dilute solutions—

$$\text{pH} = -\log a_{SO_4} - \log 2$$

and we get from (xi)—

$$\log \left(\frac{\theta_H}{1 - \theta_H}\right)^2 \left(\frac{\theta_H}{2 - \theta_H}\right) = -3\,\text{pH} - \log 2 - \frac{\log e}{RT}(2\Delta\mu_H + \Delta\mu_{SO_4}) \qquad \text{(xiv}$$

or

$$\log \frac{\theta_H}{1 - \theta_H} + \text{pH} - \frac{1}{3} \log \frac{1 - \frac{\theta_H}{2}}{1 - \theta_H} = -\frac{\log e}{3RT}(2\Delta\mu_H + \Delta\mu_{SO_4}) \qquad \text{(xiva)}$$

For hydrochloric acid the titration values of Steinhardt and Harris[3] and those of Speakman and Stott[2] were used. For all the experimental points $\log\{\theta_H/(1 - \theta_H)\} + \text{pH}$ was calculated, and $-(\Delta\mu_H + \Delta\mu_{Cl})$ determined according to (xiii). We obtain the values for $-(\Delta\mu_H + \Delta\mu_{Cl})$ of 6157 (25°c.)[3], 5968 (0°c.)[3], and 6021 (22°c.)[2] g.cal. For our purposes we interpolate 6134 g.cal. (22°c.), and thus—

$$-\frac{\log e}{RT}(\Delta\mu_H + \Delta\mu_{Cl}) = 4{\cdot}54$$

With regard to sulphuric acid, the titration curves of Speakman and Stott[2] were used, and the values of the left-hand side of (xiva) calculated for all experimental points. We obtain—

$$-\left(\Delta\mu_H + \frac{\Delta\mu_{SO_4}}{2}\right) = 5782 \text{ g.cal.}$$

and thus—

$$-\frac{\log e}{RT}(2\Delta\mu_H + \Delta\mu_{SO_4}) = 8{\cdot}55$$

For pH the values measured potentiometrically (Tables I and II) were used. The value of $\log a_{Cl}$ was calculated as—

$$\log a_{Cl} = \log c_{Cl} + \log f_{Cl}$$

where c_{Cl} is the experimental value, and the activity coefficient f_{Cl} is taken from a curve of f_{Cl} plotted against $\log I$, where I is the ionic strength of the solution—

$$I = \tfrac{1}{2} \sum_X c_X z_X^2$$

for all ions (H^+, Na^+, Cl^-, SO_4^{2-}) present in the bath. As f is assumed to be a function only of I, independent of single ion concentrations, the f_{Cl}–log I curves were plotted from tables of activity coefficient as a function of concentration in sodium chloride solutions[12], assuming that $f_{Cl}(= f_{Na}) = f_{NaCl}$. In the same manner f_{SO_4} was calculated from f_{SO_4}–log I curves that had been plotted from tables of $f_{H_2SO_4}$ in sulphuric acid

solutions[5], using the formula $f_{H_2SO_4}{}^3 = f_H{}^2 f_{SO_4}$, and $\log a_{SO_4}$ was calculated as—

$$\log a_{SO_4} = \log c_{SO_4}\text{ (experimental value)} + \log f_{SO_4}$$

Table III gives the f and $\log a$ values.

TABLE III

Activities and Activity Coefficients

Sample	pH	$-\log I$	f_H	$f_{Cl} = f_{Na}$	f_{SO_4}	$-\log a_{Cl}$	$-\log a_{SO_4}$
			A— HCl + 0·1 N-Na_2SO_4				
1	4·44	0·832	0·779	0·748	0·331	2·90	1·80
2	3·52	0·836	0·779	0·748	0·331	2·53	1·81
3	2·99	0·832	0·779	0·748	0·331	2·28	1·81
4	2·46	0·824	0·778	0·747	0·329	2·03	1·82
5	1·93	0·788	0·776	0·742	0·320	1·70	1·83
6	1·57	0·728	0·770	0·734	0·306	1·44	1·85
			B— H_2SO_4 + 0·1 N-NaCl				
1	4·62	1·000	0·797	0·767	0·378	1·14	3·19
2	3·48	0·975	0·795	0·768	0·370	1·13	2·95
3	2·98	0·995	0·797	0·770	0·376	1·16	2·91
4	2·28	0·954	0·792	0·765	0·366	1·16	2·63
5	1·92	0·889	0·784	0·756	0·346	1·17	2·36
6	1·62	0·798	0·776	0·742	0·322	1·17	2·14

As the terms on the right-hand sides of (x) and (xi) are now known, the θ values can be calculated from these equations and (xii). Because of the complicated form of the equations a method of successive approximation must be used. This is best done as follows—

We choose a value θ_H' for θ_H and calculate the quotients—

$$\alpha = \frac{\theta_{Cl}}{1 - \theta_{Cl} - \theta_{SO_4}}$$

and

$$\beta = \frac{\theta_{SO_4}}{1 - \theta_{Cl} - \theta_{SO_4}}$$

from (x) and (xi), and hence calculate—

$$\theta_{Cl} = \frac{\alpha}{1 + \alpha + \beta} \text{ and } \theta_{SO_4} = \frac{\beta}{1 + \alpha + \beta}$$

From (xii) θ_H is then calculated, and this value is plotted against the suggested θ_H' value on a graph. We make a new calculation of the same kind using another θ_H' value. The two points thus obtained are joined, and the point of intersection between this line and the line $\theta_H = \theta_H'$ is determined. Then new values of θ_H are calculated as before from θ_H' values near the point of intersection. To obtain sufficient accuracy two θ_H' values differing by 0·01 and giving points on opposite sides of the line $\theta_H = \theta_H'$ are chosen, and the final θ_H value (to three places of decimals) is determined by linear interpolation. Finally $A = \theta A_{max}$ is calculated in all cases, A_{max} being taken as 0·860 millimole per gram of dry wool[2,3]. As can be seen from Fig. 3 and 4, the agreement between theoretical and experimental plots is satisfactory, especially for the negative ions in the case of sulphuric acid titrations. For hydrogen ions the agreement is not so good, especially with hydrochloric acid. Also, if we use the experimental θ_H values and calculate the θ_{Cl} and θ_{SO_4} values from these according to (x) and (xi), equation (xii) is not at all satisfied.

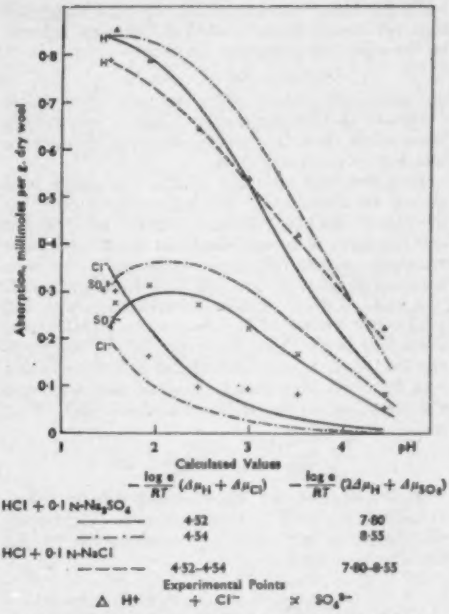

FIG. 3—Absorption of Ions by Wool from Hydrochloric Acid in presence of Salts calculated according to the Gilbert–Rideal Theory

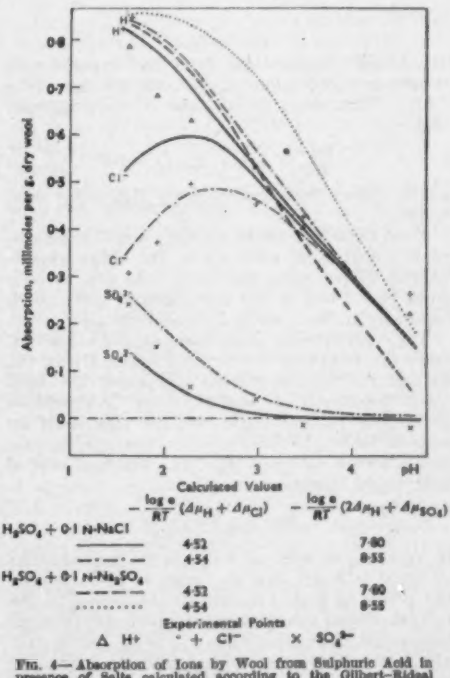

FIG. 4—Absorption of Ions by Wool from Sulphuric Acid in presence of Salts calculated according to the Gilbert–Rideal Theory

To get better agreement, it was first suggested that pH should be calculated in the same manner as the other ion activities, i.e. from—

$$\mathrm{pH} = -\log c_{\mathrm{H}} - \log f_{\mathrm{H}}$$

as these pH values differ slightly from those obtained potentiometrically. Some calculations were made, but the agreement with experiment was not so good as before.

However, the accuracy of the $\Delta\mu$ values used should be considered. For hydrochloric acid, the Steinhardt–Harris titration curves[3] at different salt concentrations were used and also the La Fleur titration curves[8]. In the calculations it has been assumed in all cases that $\mathrm{pH} = -\log a_{\mathrm{Cl}}$, which is not quite correct. Hence a comparison was also made with values of $-(\Delta\mu_{\mathrm{H}} + \Delta\mu_{\mathrm{Cl}})$ calculated according to (x) from the experimental results in the twelve titrations. But the same average value was obtained from this last calculation and from the titration curves of other authors, and so we put—

$$-\frac{\log e}{RT}(\Delta\mu_{\mathrm{H}} + \Delta\mu_{\mathrm{Cl}}) = 4{\cdot}52$$

The variation of the corresponding values for sulphuric acid is much greater. Curves by Steinhardt *et al.*[6] give 7·50 and curves by La Fleur[8] give 7·60 for—

$$-\frac{\log e}{RT}(2\,\Delta\mu_{\mathrm{H}} + \Delta\mu_{\mathrm{SO_4}})$$

In both cases the assumption that—

$$\mathrm{pH} = -\log a_{\mathrm{SO_4}} - \log 2$$

i.e. that—

$$f_{\mathrm{H}} = f_{\mathrm{SO_4}}$$

was made. Calculations from our experimental results using equation (xi) give the average value 7·81. From these calculations it was suggested that—

$$-\frac{\log e}{RT}(2\,\Delta\mu_{\mathrm{H}} + \Delta\mu_{\mathrm{SO_4}}) = 7{\cdot}80$$

which differs considerably from the value used before.

From these new values for free energy differences fresh calculations were made, the other experimental values being the same. As can be seen from Fig. 3 and 4, the agreement is quite good, especially in the case of hydrochloric acid.

The concentration of sodium ions was calculated from the condition of electrical neutrality in the bath and on the fibre. It was thus found that small quantities of sodium were absorbed. It should be of interest to investigate whether this could be responsible for the difference between experimental and observed values of A_{H}. The left-hand side of (vii) would then become—

$$\log\frac{\theta_{\mathrm{H}}}{1-\theta_{\mathrm{H}}-\theta_{\mathrm{Na}}}$$

If, now, θ_{H} is assumed to have its experimental value, it is found that θ_{Na} must be < 0 even for the points at high pH values. According to the Gilbert–Rideal theory there is a possibility of slight sodium ion absorption when $c_{\mathrm{Na}} \gg c_{\mathrm{H}}$, but as such absorption is not in agreement with our curves, we can neglect this possibility. The small excess of negative ions absorbed is then probably due to the ash content of the fibres.

Another factor to be considered is the presence of HSO_4^- ions at low pH. This must, of course, be the case with pure sulphuric acid too, and thus we can examine its effect on the titration curve for the pure acid according to Gilbert and Rideal. If Cl is replaced by HSO_4 everywhere in equations (x) and (xi) we get the appropriate equations (x*a*) and (xi*a*)—

$$\log\frac{\theta_{\mathrm{H}}}{1-\theta_{\mathrm{H}}} + \log\frac{\theta_{\mathrm{HSO_4}}}{1-\theta_{\mathrm{HSO_4}}-\theta_{\mathrm{SO_4}}} = -\frac{\log e}{RT}(\Delta\mu_{\mathrm{H}} + \Delta\mu_{\mathrm{HSO_4}}) - \mathrm{pH} + \log a_{\mathrm{HSO_4}} \quad (x\textit{a})$$

$$2\log\frac{\theta_{\mathrm{H}}}{1-\theta_{\mathrm{H}}} + \log\frac{\theta_{\mathrm{SO_4}}}{1-\theta_{\mathrm{HSO_4}}-\theta_{\mathrm{SO_4}}} = -\frac{\log e}{RT}(2\,\Delta\mu_{\mathrm{H}} + \Delta\mu_{\mathrm{SO_4}}) - 2\,\mathrm{pH} + \log a_{\mathrm{SO_4}} \quad (xi\textit{a})$$

For the dissociation—

$$HSO_4^- \rightarrow SO_4^{2-} + H^+$$

$K_a = 0{\cdot}01243$ and $\mathrm{p}K_a = 1{\cdot}9$. For pH well above 1·9 this dissociation may be neglected and the ordinary formula (xiv*a*) may be used to give the quantity $\Delta\mu_{\mathrm{H}} + \frac{1}{2}\Delta\mu_{\mathrm{SO_4}}$, which is, of course, independent of pH. For pH in the neighbourhood of and below 1·9 we may first calculate $c_{\mathrm{SO_4}}$ and $c_{\mathrm{HSO_4}}$ from the given values of K_a and c_{H}. As all activity coefficients may be determined from tables, the right-hand side of (xi*a*) is determined. As also θ_{H} is known experimentally, $\theta_{\mathrm{SO_4}}$ and $\theta_{\mathrm{HSO_4}}$ may be calculated from (xi*a*) and the condition for electrical neutrality—

$$\theta_{\mathrm{H}} = \theta_{\mathrm{HSO_4}} + 2\theta_{\mathrm{SO_4}}$$

However, these calculated values of $\theta_{\mathrm{HSO_4}}$ are negative and not usable. Thus we cannot get a more satisfactory explanation of the experimental curve by taking into account the presence of HSO_4^- ions.

Lastly the theoretical A_{H} curves for HCl + 0·1 N-NaCl and H_2SO_4 + 0·1 N-Na_2SO_4 were calculated, using equations (x) and (xi), but omitting $\theta_{\mathrm{SO_4}}$ or θ_{Cl} respectively and substituting $\theta_{\mathrm{H}} = \theta_{\mathrm{Cl}}$ or $2\theta_{\mathrm{SO_4}}$ respectively. The values of $\Delta\mu$ and pH were the same as in the previous calculations, and the values of a_{Cl} and $a_{\mathrm{SO_4}}$ were determined from the concentrations of 0·1 N. salt and acid in equilibrium and the calculated activity coefficients. The value of θ_{H} is then calculated directly from (x) for hydrochloric acid and by a rapid successive approximation from (xi) for sulphuric acid. The values (Fig. 3 and 4) show that the relation between titration curves in the presence of sodium chloride and sodium sulphate for both acids is of the same kind as that obtained from the complete titration curves (Fig. 1 and 2).

THE DONNAN INTERPRETATION

Peters and Speakman[13] have given the equation—

$$\frac{f_{\mathrm{X,int}}}{f_{\mathrm{X,ext}}}\left(\frac{a_{\mathrm{H_2O,ext}}}{a_{\mathrm{H_2O,int}}}\right)^{r_{\mathrm{X}}}\frac{[\mathrm{X}]_{\mathrm{int}}}{[\mathrm{X}]_{\mathrm{ext}}} = \lambda^2 \qquad (xv)$$

where the subscripts refer to the internal and external phases, r_X is the ratio of the partial molar volume of the ion X (of charge z) to that of water, and λ is the Donnan quotient. Like Peters and Speakman we assume that both r_X and the ratio $a_{H_2O,e}/a_{H_2O,i}$ equal unity.

If the concentration of ionic groups on the fibre calculated for the volume v is a, then we have—

—COOH	$a\theta'$
—COO⁻	$a(1-\theta')$
—NH_3^+	a

The condition for electrical neutrality in the external phase (already used for the calculation of $[Na^+]_e$ is—

$$[H^+]_e + [Na^+]_e = [Cl^-]_e + 2[SO_4^{2-}]_e + [HSO_4^-]_e$$

while for the internal phase it is—

$$a + [H^+]_i + [Na^+]_i = a(1-\theta') + [Cl^-]_i + 2[SO_4^{2-}]_i + [HSO_4^-]_i$$

or

$$a\theta' + [H^+]_i + [Na^+]_i = [Cl^-]_i + 2[SO_4^{2-}]_i + [HSO_4^-]_i \quad \text{(xvi)}$$

The conditions of chemical equilibrium for diffusible ions are—

$$\lambda = \frac{f_{H,e}[H^+]_e}{f_{H,i}[H^+]_i} = \frac{f_{Na,e}[Na^+]_e}{f_{Na,i}[Na^+]_i} = \frac{f_{Cl,i}[Cl^-]_i}{f_{Cl,e}[Cl^-]_e} = \frac{f_{HSO_4,i}[HSO_4^-]_i}{f_{HSO_4,e}[HSO_4^-]_e} = \left(\frac{f_{SO_4,i}[SO_4^{2-}]_i}{f_{SO_4,e}[SO_4^{2-}]_e}\right)^{\frac{1}{2}} \quad \text{(xvii)}$$

the values of $[HSO_4^-]$ in both phases being calculated from the dissociation constant—

$$K_a = \frac{f_H[H^+] \times f_{SO_4}[SO_4^{2-}]}{f_{HSO_4}[HSO_4^-]} \quad \text{(xviii)}$$

If A is the number of millimoles absorbed per gram of dry wool calculated on the assumption that all the liquid has the same composition as the external solution, as in our tables, and v is the volume of the internal solution per gram of dry wool, then the concentration in the internal solution will be A/v, so that—

$$\frac{A_H}{v} = a\theta' + ([H^+]_i - [H^+]_e) + ([HSO_4^-]_i - [HSO_4^-]_e) \quad \text{(xix)}$$

$$\frac{A_{Na}}{v} = [Na^+]_i - [Na^+]_e \quad \text{(xx)}$$

$$\frac{A_{Cl}}{v} = [Cl^-]_i - [Cl^-]_e \quad \text{(xxi)}$$

$$\frac{A_{SO_4}}{v} = ([SO_4^{2-}]_i - [SO_4^{2-}]_e) + ([HSO_4^-]_i - [HSO_4^-]_e) \quad \text{(xxii)}$$

We want to calculate λ from the measured external concentrations according to (xvi) and (xvii). One more equation is necessary, and the most appropriate is (xix). Thus we substitute for the internal concentrations in (xvi) and (xix) by means of (xvii) and obtain—

$$a\theta' + \frac{f_{H,e}[H^+]_e}{f_{H,i}\lambda} + \frac{f_{Na,e}[Na^+]_e}{f_{Na,i}\lambda} = \frac{f_{Cl,e}[Cl^-]_e\lambda}{f_{Cl,i}} + \frac{f_{HSO_4,e}[HSO_4^-]_e\lambda}{f_{HSO_4,i}} + \frac{2f_{SO_4,e}[SO_4^{2-}]_e\lambda^2}{f_{SO_4,i}} \quad \text{(xvia)}$$

$$\frac{A_H}{v} = a\theta' + [H^+]_e\left(\frac{f_{H,e}}{f_{H,i}\lambda} - 1\right) + [HSO_4^-]_e\left(\frac{f_{HSO_4,e}\lambda}{f_{HSO_4,i}} - 1\right) \quad \text{(xixa)}$$

If, now, $a\theta'$ is eliminated between (xvia) and (xixa) and terms are rearranged, we get—

$$\frac{2f_{SO_4,e}[SO_4^{2-}]_e}{f_{SO_4,i}}\lambda^3 + \left(\frac{f_{Cl,e}[Cl^-]_e}{f_{Cl,i}} + \frac{2f_{HSO_4,e}[HSO_4^-]_e}{f_{HSO_4,i}}\right)\lambda^2 - \left([H^+]_e + [HSO_4^-]_e + \frac{A_H}{v}\right)\lambda - \frac{f_{Na,e}[Na^+]_e}{f_{Na,i}} = 0 \quad \text{(xxiii)}$$

If the concentration of HSO_4^- ions is negligible, equation (xxiii) simplifies to—

$$2\frac{f_{SO_4,e}[SO_4^{2-}]_e}{f_{SO_4,i}}\lambda^2 + \frac{f_{Cl,e}[Cl^-]_e}{f_{Cl,i}}\lambda^2 - \left([H^+]_e + \frac{A_H}{v}\right)\lambda - \frac{f_{Na,e}[Na^+]_e}{f_{Na,i}} = 0 \quad \text{(xxiv)}$$

For v the value 0·285 ml. per gram of dry wool was used[13]. As the salt concentration is 0·1 N., we can assume that the values of λ do not differ very greatly from 1·0. Thus the f values of the different ions should be the same in both external and internal solutions, and we may assume for all ions that—

$$\frac{f_e}{f_i} = 1$$

Thus all quantities in (xxiv) are known from Tables I and II. In (xxiii) $[Cl^-]_e$ and $[Na^+]_e$ have the same values as in (xxiv), and $[SO_4^{2-}]_e$ and $[HSO_4^-]_e$ are calculated from (xviii), assuming their sum to be equal to the measured value of c_{SO_4}. A correction to c_H for the presence of HSO_4^- is then made to obtain the value of $[H^+]_e$ in (xxiii).

The values of λ are now calculated from (xxiii) or (xxiv). We easily find that in all cases the three roots of these equations are real, but two of them are negative and not usable. The equations are solved by approximation and interpolation methods. As seen from Table IV (first approximation) the λ values thus obtained are appreciably greater than 1, especially for sulphuric acid titrations. Thus our assumption of f ratios of unity is a rather rough approximation. Using equations (xvii), we now calculate the concentrations in the internal solution (f values being disregarded), and hence the ionic strength—

$$I_i = \tfrac{1}{2}([H^+]_i + [Na^+]_i + [Cl^-]_i + 4[SO_4^{2-}]_i)$$

From our f–log I curves the corresponding f values are determined (Table IV). The quotients f_e/f_i are then calculated, and these values substituted in (xxiv), the other constants being the same as before. New λ values are now calculated (second approximation). They are significantly smaller than the first values (Table IV). If the process of calculating ionic strength and activity coefficients in the internal solution is repeated once more, and these new values are substituted in (xxiv), we get a new

TABLE IV

Calculated Donnan Quotients and Internal Activity Coefficients

pH	$\lambda = e^{VF/RT}$				Values of f used in 3rd Approximation			
	HSO_4^- considered	HSO_4^- neglected			$-\log I_i$	$f_{H,i}$	$f_{Cl,i} = f_{Na,i}$	$f_{SO_4,i}$
		1st Approximation	2nd Approximation	3rd				
			A— HCl + 0·1 N-Na_2SO_4					
4·44	2·92	2·91	2·13	2·23	0·062	0·797	0·656	0·190
3·52	4·00	3·96	2·79	2·76	− 0·184	0·914	0·652	0·159
2·99	4·64	4·40	3·04	3·03	− 0·287	1·013	0·662	0·149
2·46	5·42	4·92	3·25	3·24	− 0·360	1·098	0·677	0·141
1·93	7·04	5·40	3·57	3·57	− 0·443	1·260	0·701	0·137
1·57	8·70	5·51	3·73	3·73	− 0·475	1·330	0·711	0·136
			B— H_2SO_4 + 0·1 N-NaCl					
4·62	6·82	6·82	6·65	5·69	0·214	0·768	0·668	0·217
3·48	9·36	9·30	7·07	7·04	− 0·018	0·819	0·652	0·178
2·98	11·65	11·70	8·17	8·14	− 0·163	0·900	0·651	0·161
2·28	11·24	10·28	6·90	6·90	− 0·273	0·996	0·662	0·150
1·92	10·32	8·18	5·53	5·52	− 0·336	1·065	0·671	0·142
1·62	10·13	6·95	4·76	4·73	− 0·415	1·190	0·691	0·138

set of λ values (third approximation) that is only slightly different from the previous set.

The absorbed amounts of different ions are now calculated according to (xvii), (xx), (xxi), and (xxii)—

$$\frac{A_{Na}}{v} = [Na^+]_0 \left(\frac{f_{Na,e}}{f_{Na,i}\lambda} - 1 \right) \qquad (xx a)$$

$$\frac{A_{Cl}}{v} = [Cl^-]_0 \left(\frac{f_{Cl,e}\lambda}{f_{Cl,i}} - 1 \right) \qquad (xxi a)$$

$$\frac{A_{SO_4}}{v} = [SO_4^{2-}]_0 \left(\frac{f_{SO_4,e}\lambda^2}{f_{SO_4,i}} - 1 \right) \qquad (xxii a)$$

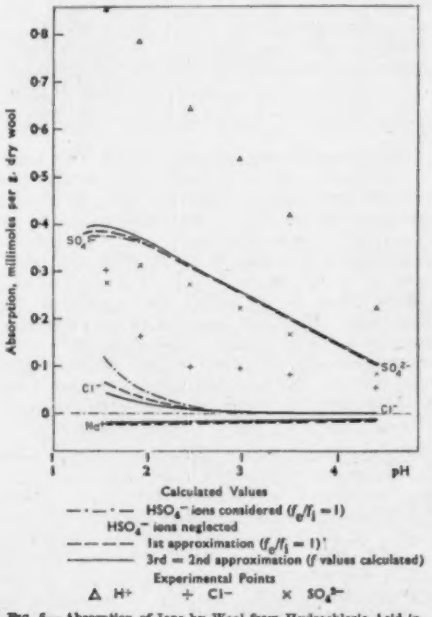

FIG. 5— Absorption of Ions by Wool from Hydrochloric Acid in presence of 0·1 N. Sodium Sulphate calculated according to the Donnan Theory

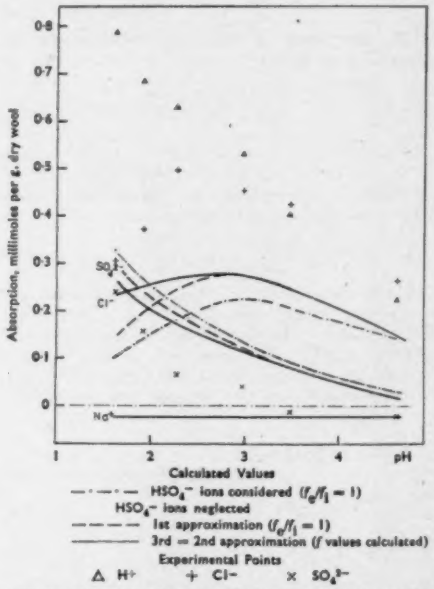

FIG. 6— Absorption of Ions by Wool from Sulphuric Acid in presence of 0·1 N. Sodium Chloride calculated according to the Donnan Theory

From Fig. 5 and 6 we see that the calculated absorption is in qualitative agreement with the experimental values, but that the quantitative agreement is very poor. For hydrochloric acid as well as sulphuric acid the absorption of Cl^- ions is too small and that of SO_4^{2-} ions too great. Of course, there are some uncertainties in this calculation— firstly in the determination of activity coefficients, secondly in the approximation of equation (xv), and thirdly in using the value v = 0·285 ml./g.

The activity coefficients were calculated from the calculated ionic concentrations in the internal

solutions, regardless of the activities of the ionic groups of the fibre. However, in fact only very small changes in absorption are produced by quite considerable changes in f and thus in λ, as is seen from a comparison between the first and second approximations (Fig. 5 and 6), and there is no reason to suppose that a further change in activity will greatly change the calculated A values. We may also suppose that the charged $-NH_3^+$ and $-COO^-$ groups of the fibre contribute to the ionic strength. This contribution ΔI_1 should lie within the range—

$$0 < \Delta I_1 < \tfrac{1}{2}[\alpha + \alpha(1 - \theta')]$$

A calculation of I_1 is carried out using the maximum value of ΔI_1. The corresponding f_1 values are calculated and substituted in (xxiv), other figures being the same as before. For sulphuric acid plus sodium chloride we get the values in Table V. In calculating f_0 here we have also considered the existence of HSO_4^- ions. These values are not very different from those plotted in Fig. 6, the agreement with experiment being rather worse than before. Nor may we assume that a better approximation for $(a_{H_2O\cdot e}/a_{H_2O\cdot 1})^{\nu x}$ in (xv) will greatly affect the A values, as this factor may be incorporated in the f quotients. If v is taken 100 times too big, the calculated A values are still in qualitative agreement with the experimental values. Thus the uncertainty in the value of v employed certainly cannot influence the results.

TABLE V

Absorptions calculated according to the Donnan Theory for H_2SO_4 + 0·1 N-NaCl, taking into account the $-NH_3^+$ and $-COO^-$ Groups of the Fibre

$I_1 = \frac{1}{2}\{[H^+]_1 + [Na^+]_1 + [Cl^-]_1 + 4[SO_4^{2-}]_1 + \alpha(2 - \theta')\}$

pH	$-\log I_1$	λ	A_{Na}	A_{Cl}	A_{SO_4}
4·62	− 0·496	5·59	− 0·023	0·135	0·044
2·28	− 0·580	6·57	− 0·023	0·148	0·229
1·62	− 0·634	4·45	− 0·020	0·085	0·340

As we have no figures on the influence of the fixed charges on the fibre on the activity coefficients in the internal solution, we may make other calculations from (xxi*a*) and (xxii*a*). Assuming that not only $[Cl^-]_e$, $[SO_4^{2-}]_e$, $f_{Cl,e}$, $f_{SO_4,e}$, but also A_{Na} and A_{Cl} have their experimental values (Tables I–III), we may calculate the values of $f_{Cl,1}$ and $f_{SO_4,1}$, using λ values calculated earlier (third approximation in Table IV) and $v = 0{\cdot}285$ (Table VI). Most of these f values are definitely smaller than any determined for Cl^- and SO_4^{2-} solutions, but perhaps not improbably small. However, in most cases the $f_{Cl,1}$ values are definitely smaller than the corresponding $f_{SO_4,1}$ values, which again makes the quantitative Donnan interpretation very doubtful.

TABLE VI

Calculated Internal Activity Coefficients from Experimental Absorption Values

pH	$f_{Cl,1}$	$f_{SO_4,1}$
HCl + 0·1 N-Na_2SO_4		
3·52	0·028	0·188
2·46	0·085	0·158
1·57	0·121	0·193
H_2SO_4 + 0·1 N-NaCl		
3·48	0·329	~0
2·28	0·264	0·473
1·62	0·277	0·188

If the HSO_4^- ions are considered, the titration curves are displaced to some extent at low pH, especially in the case of the sulphuric acid titration (Fig. 5 and 6). It should also be noted that calculation gives a "desorption" of sodium ions. As mentioned earlier, we found no experimental sign of this, but on the contrary some "absorption" of Na^+. However, the figures are so small that these differences are not significant.

To compare Gilbert–Rideal values and Donnan values, the Donnan absorptions of Na^+, Cl^-, and SO_4^{2-} for certain points were also calculated using the previously calculated Gilbert–Rideal values for A_H instead of the experimental values. This did not change the absorbed quantities significantly (Table VII).

TABLE VII

Absorptions calculated according to the Donnan Theory but using A_H Values calculated according to the Gilbert–Rideal Theory (Fig. 3 and 4)

pH	λ (HSO_4^- neglected)	A_{Na}	A_{Cl}	A_{SO_4}
HCl + 0·1 N-Na_2SO_4				
3·52	2·48	− 0·015	0·002	0·159
2·46	3·37	− 0·019	0·010	0·334
1·57	3·68	− 0·020	0·039	0·385
H_2SO_4 + 0·1 N-NaCl				
4·62	4·51	− 0·021	0·113	0·017
2·98	8·11	− 0·023	0·223	0·142
1·92	5·90	− 0·022	0·146	0·302

CONCLUSIONS

The above calculations show that both the Gilbert–Rideal theory and the Donnan theory can be used in a qualitative manner to describe the ion-binding properties of wool in the presence of strong acids. But from a more quantitative viewpoint the Gilbert–Rideal theory is in better agreement with experiment than the Donnan theory. This means that the negative ions are not distributed at random in the internal solution of the fibres, but are more selectively, and more or less firmly, bound to positive sites in the fibre. There are some doubts about the accuracy of the former theory for describing titration curves at high salt concentration and high pH, made by Peters and Speakman[13]. However, in this region the discrepancies are not so significant as to disprove the validity of either theory. And besides the effect of using activities instead of concentrations, there is also a possibility of selective sodium ion absorption, that could account for these discrepancies. Peters and Speakman state further that the compound $R{\cdot}NH_3Cl$ is electronically impossible. We have no means of determining the effect of a non-homogeneous

localized positive ion distribution on the activity of free ions. To explain the experimental results from free ionic concepts it is not sufficient to postulate an extraordinary absolute decrease of activity coefficients (see above) but it is necessary also to assume that these coefficients are changed relatively to each other ($f_{Cl} < f_{SO_4}$). It is, of course, not self-evident that the Fowler–Guggenheim equation for molecules can be applied to ions as was done by Gilbert and Rideal (v), but its usefulness is confirmed by the agreement with experiment.

These experiments, however, ought to be completed by titrations with mixtures of hydrochloric and sulphuric acids. The present results are not decisive regarding the validity of the Gilbert–Rideal theory as compared with the Donnan theory, as there are some experimental uncertainties, e.g. the "Na-absorption" correction, but the trend of the calculations is clear*.

The author wishes to thank Professor Nils Gralén, head of the Swedish Institute for Textile Research, for his encouraging interest in this work and Miss Birgit Johansson for her careful help with experiments and some calculations. He also thanks Dr. L. Peters, of the University of Leeds, who has read the manuscript and made valuable suggestions.

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* A paper on sulphuric acid absorption has recently been published by D. Donovan and P. Larose[16], in which no significant influence of the presence of sodium sulphate in different amounts was found on the absorption of hydrogen ions. They used, however, low pH (~ 2·3), where the influence is small according to our curves (Fig. 2). To get rid of alkaline ash they pretreated their wool samples in weak acetic acid. Their results are compared with both the Gilbert–Rideal and the Donnan theories, and they draw the conclusion that the latter theory explains the results more satisfactorily than the former. However, the differences are small and probably not significant, and the authors emphasize the importance of more experimental work.

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The Reaction of Acrylonitrile with Macromolecular Hydroxy Substances
I—A General Survey of the Reaction

J. H. MacGregor

The interaction of acrylonitrile with the reactive hydrogen atoms of the hydroxy groups of macromolecular organic substances such as cellulose, starch, and polyvinyl alcohol is described. It is shown that water-insoluble (caustic alkali-soluble), water-soluble, and acetone-soluble β-cyanoethyl ethers are produced by modifying the molar amounts of acrylonitrile reacting with these macromolecular hydroxy substances. The properties of these partly and fully cyanoethylated ethers are reviewed and probable industrial applications suggested, with special reference to the textile field.

The nature of the rather complex reactions which occur when acrylonitrile reacts with aqueous solutions of these high polymers in the presence of a caustic alkali as catalyst is discussed and explained. The stepwise course of the alkaline hydrolysis of the β-cyanoethyl ethers is also described.

Introduction

Acrylonitrile (vinyl cyanide $CH_2{:}CH{\cdot}CN$) was first prepared by Moureu[1], who applied Dumas's[2] classical method of preparing organic nitriles by reaction of the corresponding amide with phosphorus pentoxide. The distillation of acrylamide with phosphorus pentoxide yielded acrylonitrile by dehydration—

$$CH_2{:}CH{\cdot}CO{\cdot}NH_2 \xrightarrow{P_2O_5} CH_2{:}CH{\cdot}CN + H_2O$$

At the same time Moureu found that dehydration of ethylene cyanohydrin with phosphorus pentoxide also yielded acrylonitrile—

$$HO{\cdot}CH_2{\cdot}CH_2{\cdot}CN \xrightarrow{P_2O_5} CH_2{:}CH{\cdot}CN + H_2O$$

A study of the literature from the time of Moureu's discovery indicates that very little interest was shown in the chemical behaviour of acrylonitrile for at least forty years. The quest in the early nineteen-thirties for substances capable of yielding highly polymeric materials and the desire, especially in Germany, for substances which, when copolymerized with butadiene, would produce valuable synthetic rubbers led to the consideration of acrylonitrile. Investigation had shown that butadiene, when polymerized alone by the emulsion technique, yielded products which were certainly rubberlike in nature, but they fell far short of natural rubber in every respect. It was established, however, that butadiene could be copolymerized with certain vinyl derivatives such as vinylbenzene (styrene $CH_2{:}CH{\cdot}C_6H_5$) and acrylonitrile. When polymerized alone, styrene and acrylonitrile both yield rather brittle polymers,

but on copolymerization with butadiene they cause an alteration in the intermolecular forces sufficient to produce polymers possessing the desired mechanical characteristics. The best known examples of these copolymers are the Buna S (GR–S) and the Buna N (GR–N) rubbers, which were originally developed in Germany but which were[2] manufactured in substantial quantities in America during the recent war. The ratio of styrene or acrylonitrile to butadiene in these most useful copolymers is about 1 : 4 by weight. Butadiene–acrylonitrile copolymers of the Buna N type are characterized by their outstanding resistance to swelling in petrol, aliphatic hydrocarbons, or lubricating oils. Furthermore, their resistance to oxidation and decomposition when exposed to heat is reported to be very good, and they are less permeable to air and gases than is natural rubber.

Recently, fibres have been produced by spinning solutions of polyacrylonitrile and copolymers of acrylonitrile and other vinyl derivatives such as vinyl chloride and styrene. Indeed, fibres and films produced from polyacrylonitrile and its copolymers have already appeared on the market. They cover a wide range of properties from rigid, strong, and tough fibres to soft, pliable, and elastic films, and possess high resistance to chemical attack as well as to degradation by oxidation, sunlight, and bacteria.

In view of its growing importance as a raw material it is not surprising that acrylonitrile is now manufactured on a large scale, especially in America. Moreover, there is evidence from recent reports[3] that in Germany, too, acrylonitrile was produced in vast quantities, at any rate until the end of the recent war.

The chief method in use in America for manufacturing acrylonitrile is, quite naturally, based on ethylene. This is bubbled through hypochlorous acid to yield ethylene chlorohydrin, which with sodium cyanide gives the cyanohydrin, from which acrylonitrile is obtained on dehydration. The following scheme represents the main stages in the preparation—

$$CH_2{:}CH_2 + HClO(aq.) \longrightarrow HO{\cdot}CH_2{\cdot}CH_2{\cdot}Cl \quad (a)$$

$$HO{\cdot}CH_2{\cdot}CH_2{\cdot}Cl + NaCN \longrightarrow HO{\cdot}CH_2{\cdot}CH_2{\cdot}CN + NaCl \quad (b)$$

$$HO{\cdot}CH_2{\cdot}CH_2{\cdot}CN \xrightarrow[\text{Heat}]{KHSO_4} CH_2{:}CH{\cdot}CN + H_2O \quad (c)$$

An interesting account of the semi-technical preparation of ethylene cyanohydrin from ethylene chlorohydrin and of the effect of numerous dehydrating agents on the cyanohydrin, so far as these affect the purity and yield of the resulting acrylonitrile, has been given recently by Hands and Walker[4]. As a result of their studies these authors suggest that aluminium powder is the most satisfactory dehydrating agent.

Acrylonitrile appears to be manufactured in Germany by two different routes—

$$\underset{\diagdown O \diagup}{CH_2{-}CH_2} + HCN \rightarrow HO{\cdot}CH_2{\cdot}CH_2{\cdot}CN \rightarrow CH_2{:}CH{\cdot}CN + H_2O \quad (i)$$

$$HC{:}CH + HCN \rightarrow CH_2{:}CH{\cdot}CN \quad (ii)$$

In the former process, which is the older one, ethylene oxide reacts with hydrogen cyanide in the presence of an alkaline catalyst, preferably diethylamine and a little sodium hydroxide, and water, which is necessary for the reaction to proceed at reasonable speed. The ethylene cyanohydrin so obtained is then dehydrated semi-continuously in the liquid phase in the presence of bauxite or magnesium carbonate as catalyst[5] (cf. however Hands and Walker[4]).

In the second process, which is stated to be the cheapest method of synthesis so far developed, a mixture of acetylene, hydrogen cyanide, and nitrogen is circulated through a tower containing an aqueous ammonium chloride–cuprous chloride mixture, which acts as the catalyst. The reaction between acetylene and hydrogen cyanide is exothermic, sufficient heat being liberated to maintain the catalytic mixture at 80°C. (the optimum reaction temperature), so that no external heating is necessary. It is stated that optimum yields are obtained when the molar ratio of acetylene to hydrogen cyanide is 10 : 1. The catalyst, which is of the Nieuwland[6] type, is made by forming an equimolar saturated aqueous solution of ammonium and cuprous chlorides at 40°C. During the reaction the pH of the solution is maintained at 3·5—this condition is reported to be important.

The principal physical properties of acrylonitrile have been listed by Davis and Wiedeman[7]. It is a water-white mobile liquid of density 0·8004 g./c.c. at 25°C., which boils at 77–78°C. and possesses a rather unpleasant odour. As the vapours of acrylonitrile are somewhat poisonous, it is advisable when working with this substance to do so in well ventilated rooms.

The work of Bruson *et al.*[8] from about 1942 onwards has shown that the ethylene linkage in acrylonitrile enters into many addition reactions not normally shown by an olefinic (–C=C–) bond. It is well known that the double bond in olefins is unreactive to anionoid reagents because it cannot act as an electron acceptor. However, when a substituent is present which influences the electronic configuration of the molecule by conjugation, the –C=C– bond becomes sensitized to anionoid additions, and the substituent group is said to exercise an *electromeric* (*E*) effect (cf. Dewar[9]). In acrylonitrile we have a typical example of such a condition, the nitrile group in this instance exercising a positive electromeric (+ *E*) effect. As a result of this additive property, acrylonitrile condenses with a wide range of organic substances possessing reactive hydrogen atoms, such as amines, alcohols, etc. These addition reactions of acrylonitrile are catalysed by alkaline condensing agents such as the caustic alkalis and quaternary ammonium hydroxides, and are typical Michael reactions. Thus an anionoid reagent X^- will add to acrylonitrile according to the following mechanism—

$$\overset{\curvearrowright}{X}^- + CH_2{=}\overset{\curvearrowright}{C}H{-}CN \longrightarrow X{-}CH_2{-}\bar{C}H{-}CN \xrightarrow{H^+} X{-}CH_2{-}CH_2{-}CN$$

The ease of addition should vary with the anionoid activity of X^-. Thus amines or carbanions should react more easily than alcohols, and

alkoxide RO^- ions more readily than alcohols themselves. This accounts for the base catalysis of the alcohol additions.

It has been shown by MacGregor and Pugh[10] that in the presence of small amounts of strong alkaline condensing agents aliphatic alcohols readily add to acrylonitrile to give β-alkoxypropionitriles—

$$R{\cdot}OH + CH_2{:}CH{\cdot}CN \rightarrow R{\cdot}O{\cdot}CH_2{\cdot}CH_2{\cdot}CN$$

In the present series of papers the reaction of acrylonitrile with the hydroxy groups of certain macromolecular substances, such as cellulose, starch, and polyvinyl alcohol, will be discussed.

Reaction of Acrylonitrile with Cellulose

The fundamental chemical unit of cellulose is the glucose residue $C_6H_{10}O_5$[11]. These glucose units have a ring structure and are linked together by primary valency bonds[12]. They determine the chemical behaviour of cellulose and account e.g. for the fact that cellulose is easily wetted and swells in water. Owing to the presence of three hydroxy groups per glucose residue, capable of reacting in the same way as the hydroxy groups of alcohols, cellulose readily forms triesters and triethers.

Under suitable conditions some or all the hydroxy groups in cellulose can be cyanoethylated by reaction with acrylonitrile. In most chemical reactions involving cellulose it is desirable, in order to obtain uniformly substituted derivatives, that the cellulose be in solution at the start or pass into solution during the early stages of the reaction. This is particularly true in the case of the cyanoethylation of cellulose. For example, low-substituted cyanoethyl cellulose ethers can be obtained by the reaction of acrylonitrile with alkali cellulose of a fairly low degree of polymerization, but the products are not homogeneous. The cyanoethyl cellulose ethers are more homogeneous if the reaction is performed in the solution phase.

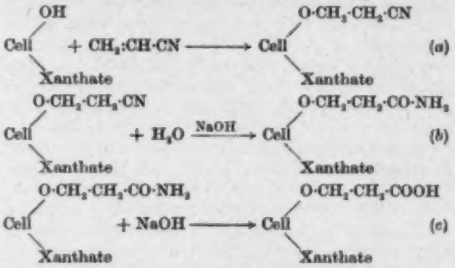
Nevertheless, Bock and Houk[13] have reported that low-substituted, water-insoluble, caustic alkali-soluble, carboxyethyl cellulose ethers are obtained by reaction of cellulose, in finely divided or fibrous form, at 5–35°C. with acrylonitrile (0·2–0·5 mol./glucose unit) in the presence of 20–30% aqueous solutions of caustic alkalis or quaternary ammonium hydroxides as catalysts. When the molar ratio of acrylonitrile to cellulose is 1–2, water-soluble carboxyethyl celluloses are obtained. These authors also claim that, when the molar ratio is > 2, cyanoethyl celluloses soluble in organic solvents are obtained[14].

In the experiments described in this section, viscose (a solution of sodium cellulose xanthate in dilute aqueous sodium hydroxide) is used as the source of cellulose. Normal viscose contains approx. 8% of cellulose and 6% of sodium hydroxide. The addition of acrylonitrile to viscose causes initially, as has been described previously[15], a very rapid colour change in the viscose, due to the combination of acrylonitrile with the elements of hydrogen sulphide in alkaline solution, with formation of $\beta\beta'$-thiodipropionitrile (bis-β-cyanoethyl sulphide)—

$$CN{\cdot}CH{:}CH_2 + H_2S + CH_2{:}CH{\cdot}CN \rightarrow CN{\cdot}CH_2{\cdot}CH_2{\cdot}S{\cdot}CH_2{\cdot}CH_2{\cdot}CN$$

These side-reactions are complete in, say, five to fifteen minutes, but over a period of hours the acrylonitrile adds to the free hydroxy groups of the sodium cellulose xanthate.

The reaction between viscose and acrylonitrile consists of at least three consecutive steps—



This stepwise form of reaction makes it extremely difficult, if not impossible, to evaluate the reaction kinetics. The reaction is conveniently followed by determining the nitrogen content of the cellulose ether isolated after removal of the xanthate groups by acidification[16]. This gives the total quantity of nitrogen fixed as cyanoethyl and carbamylethyl groups but does not differentiate between the two.

The reaction is very sensitive to temperature changes, and Fig. 1 and 2 show this effect when different molar amounts of acrylonitrile are used. No indication of the extent of reaction (*b*) is given by noting the amount of nitrogen present in the cellulosic product. The graphs merely show the interplay of reactions (*a*) and (*b*) and reaction (*c*). So far only infra-red absorption spectra data are available to show the existence of reaction (*b*), and these are not quantitative. The water-soluble and some of the water-insoluble, alkali-soluble ethers show a band at about 1667 cm.$^{-1}$, which is to be attributed to the valency vibration of the carbonyl group of an amide residue (cf. Happey, MacGregor, and Trotter[17]).

Increasing the sodium hydroxide content of the viscose increases the rates of both reactions (*a*) and (*c*), the net result being a lower degree of cyanoethylation and lower stability of the product. It is, however, possible at lower temperatures (10–20°C.), because of the lower rate of hydrolysis, to take advantage of the increased reaction rates by using viscoses of a high sodium hydroxide content.

There is evident a tendency for the reaction to be confined to the cyanoethylation of two of the three hydroxy groups in the glucose unit. Even with 20 moles of acrylonitrile to 1 molar anhydroglucose unit in viscose, a degree of substitution of 2·0 cyanoethyl groups per anhydroglucose unit is barely reached. This may be due either to blocking by xanthate groups or to the hydrolysis (*c*) preventing the cyanoethylation (*a*) from building up to this level.

As, however, the various factors influencing the reaction between viscose and acrylonitrile have been fully discussed previously (cf. MacGregor and

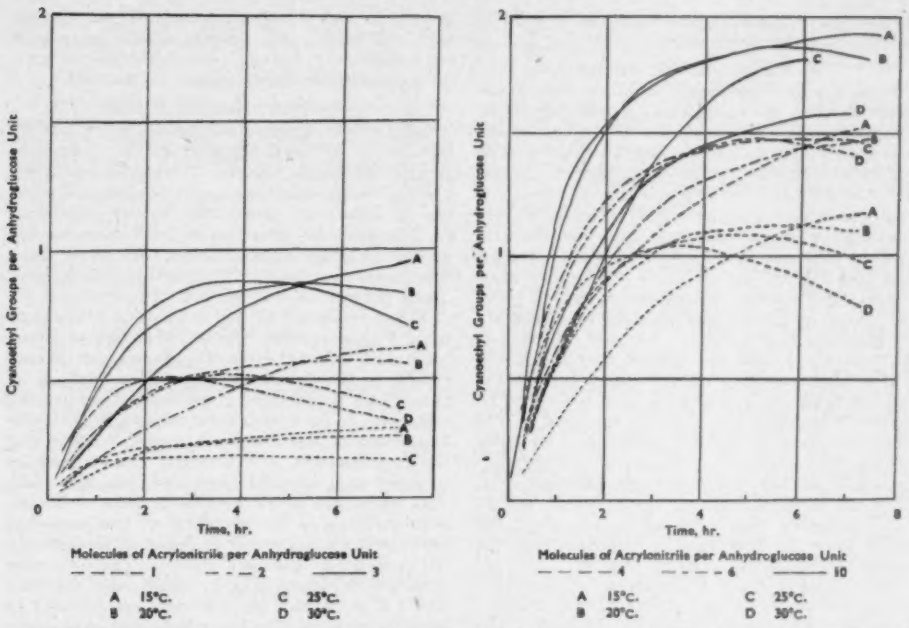


FIG. 1 and 2—Effect of Temperature on the Rate of the Viscose-Acrylonitrile Reaction with Various Molar Proportions of Acrylonitrile

Pugh[18]), it will be sufficient here to indicate briefly the nature of the cyanoethyl cellulose ethers obtained and to enumerate their properties. In the main, two types are obtained—

(*a*) WATER-INSOLUBLE, ALKALI-SOLUBLE ETHERS

When the molar ratio of acrylonitrile to anhydroglucose in viscose is 0·5–1·2, cyanoethyl celluloses are obtained which are insoluble in water but soluble in dilute aqueous solutions of the caustic alkalis and certain quaternary ammonium hydroxides. These ethers contain 0·2–0·3 cyanoethyl group per anhydroglucose unit, and can be spun, as described in Part II (p. 78), into yarns which swell strongly but do not dissolve in water. They have a water imbibition of 200–300% and quickly dissolve in 1·25% aqueous sodium hydroxide solution. These yarns offer possibilities as "scaffolding" threads for cellulosic yarns such as cotton.

The ethers of this group can also be obtained in the form of irregular fibrous lumps, which dissolve readily in dilute aqueous solutions of sodium hydroxide. Such solutions can be used for the fixation of pigments, as permanent finishing agents for textiles, as thickeners for printing pastes, for the production of novelty print effects, and for the manufacture of non-woven fabrics[19].

The following procedure has been found to be satisfactory for preparing solutions of these ethers in sodium hydroxide solution—To prepare e.g. 10 litres of a 5% solution of the cyanoethyl cellulose ether in 3% sodium hydroxide solution, 500 g. of the ether is soaked in 8 litres of cold water for half-an-hour. Sodium hydroxide flakes (300 g.) are dissolved in 1 litre of water, and the solution is added to the water-soaked cyanoethyl cellulose while the whole is thoroughly stirred. When complete solution has been effected (usually in less than 15 min.), the volume is made up to 10 litres with water. This solution can, if desired, be diluted with 3 times its own volume of water without precipitation of the cyanoethyl ether.

Stronger solutions of cyanoethyl celluloses of this type can be prepared similarly, e.g. an 8% solution in 5% caustic soda, but the cyanoethyl celluloses of this group are not readily soluble in aqueous sodium hydroxide solutions of greater than 10% strength. They are, however, readily soluble in strong aqueous solutions of certain inorganic salts, such as e.g. 25% ammonium thiocyanate, 30% sodium thiocyanate, and 50% zinc chloride, 4% solutions of the ether being obtainable. The ease and speed with which solutions of these cyanoethyl celluloses in cold aqueous sodium hydroxide may be prepared is one of their main characteristics.

Details of the application of such solutions to Fibro (spun rayon) fabrics have been given elsewhere[20]. In general, wash-fast, linen-like finishes are produced. Subjecting Fibro fabrics finished in this way to subsequent mechanical treatments such as hot or cold calendering improves their handle and appearance still further. The use of these alkaline solutions of cyanoethyl cellulose ethers in pigment fixation indicates that padding is very even and the colour yield is good. Furthermore,

the pigmented fabric, in general, shows very little change in shade on soaping.

(*b*) WATER-SOLUBLE ETHERS

Water-soluble cyanoethyl cellulose ethers are obtained when the molar ratio of acrylonitrile to anhydroglucose in viscose is 1·5–4·0. These ethers are soluble in acidic, neutral, and alkaline aqueous solutions. They are normally purified by dialysis and can be obtained in a dry state by precipitation with ethanol or acetone. They contain 0·7–1·0 cyanoethyl group per anhydroglucose unit. Neutral aqueous solutions of the ethers are stable even on long standing and are resistant to microbiological attack. Unlike aqueous solutions of methyl cellulose, those of the cyanoethyl cellulose ethers are not gelatinized on heating. Aqueous solutions of the cyanoethyl celluloses deposit very tough and flexible films on drying; these films are transparent and colourless, and possess a high resistance to organic solvents. The aqueous solutions of the ethers are good emulsifying agents and are compatible with aqueous solutions of the paraffin-chain salts and non-ionogenic surface-active agents. They are useful as sizes for textile yarns, and in this connection they offer advantages over the starch sizes in their ease of removal from the woven fabrics in the scouring process.

When the molar ratio of acrylonitrile to anhydroglucose in viscose exceeds 4, a second series of water-insoluble, alkali-soluble ethers is obtained. The solubility of these in cold aqueous sodium hydroxide solutions decreases as the degree of substitution increases. On the other hand, as the latter increases, the solubility in dilute aqueous acetone or aqueous alcohol increases, until, with a substitution of 2 cyanoethyl groups per anhydroglucose unit, the ethers are soluble in 50 : 50 (by vol.) acetone–water mixtures.

In viscose the cellulose chains are well dispersed, and cyanoethylation will occur evenly along the chain. Thus, when the viscose–acrylonitrile reaction mixture is acidified, the chains will be held apart by the bulky cyanoethyl groups, preventing full hydrogen bonding between the adjacent hydroxyl groups and hydrogen atoms as in viscose rayon yarn. These free hydroxy groups are hydrophilic, and a balance will be set up: as the degree of cyanoethylation increases, the products first become water-soluble; and then, as more hydroxy groups are blocked by cyanoethylation, the hydrophilic nature of the product gradually disappears, and it ceases to be water-soluble. It has been found that, when large molar proportions of acrylonitrile are used, water-soluble products are formed in the very early stages of the reaction, but that by the end of one hour the products are water-insoluble. The reaction of acrylonitrile with viscose, in any molar ratio, follows the same course, the only difference being of rate. With more than four moles of acrylonitrile per anhydroglucose unit of viscose, the reaction mixture separates into two phases after about one hour, giving lumps of cellulosic material and an aqueous acrylonitrile liquid. This is because the degree of cyanoethylation has passed the stage at which the product is soluble in the concentration of alkali present in the reaction mixture. When viscoses with high caustic soda contents are used, even with ten moles of acrylonitrile per anhydroglucose unit, no separation into two phases is observed.

(*c*) SOLVENT-SOLUBLE ETHERS

Cyanoethyl cellulose ethers soluble in dry acetone have never yet been prepared by the reaction of acrylonitrile with viscose. The presence of an average of one xanthate group per two anhydroglucose units would prevent the reaction proceeding further than the introduction of 2·5 cyanoethyl groups per anhydroglucose unit. In actual practice, however, a limit of 2 cyanoethyl groups introduced per glucose unit has not been exceeded.

X-Ray analysis[21] of highly oriented fibres spun from acetone-soluble cyanoethyl cellulose ethers containing 2·75–3·0 cyanoethyl groups per glucose residue suggests that the crystalline portions of these fibres, unlike those of natural and regenerated celluloses, have a structure consistent with the hypothesis of one chain per unit cell containing three consecutive triscyanoethyl glucose residues arranged in a threefold spiral along the fibre axis. This rearrangement of the glucose units within the cellulose chain in the micelle when triscyanoethyl cellulose is formed would no doubt be hindered by the presence of xanthate groups. The cellotriose structure of almost fully cyanoethylated cellulose would also explain the difficulty encountered in introducing more than two cyanoethyl groups into regenerated cellulose yarns without loss of fibre structure. Indeed, these heterogeneously cyanoethylated fibres, containing two groups per glucose residue, show a crystal structure very similar to that of hydrate cellulose.

When regenerated cellulose[23] or a low-substituted water-insoluble or water-soluble cyanoethyl cellulose[23] is swollen in a weak (1–2%) aqueous solution of sodium hydroxide, squeezed free of surplus liquor, and treated with excess of acrylonitrile at about 80°C., the nitrogen content gradually increases until all three hydroxy groups are substituted and the product becomes soluble in acetone. The cellulose at no stage becomes water-soluble, indicating that the reaction is heterogeneous and cyanoethylation is uneven, the outside chains being attacked before those on the inside. The cellulose ethers of this group contain 2·5–3·0 cyanoethyl groups per anhydroglucose unit and are soluble in acetone, acrylonitrile, dimethylformamide, methyl formate, and β-ethoxypropionitrile. Fibres can be spun and films cast from their solutions in acetone. Unlike the water-insoluble (caustic alkali-soluble) and the water-soluble cyanoethyl cellulose ethers, as well as the other cellulose ethers of industrial importance, which possess poor resistance to photodegradation, the acetone-soluble cyanoethyl celluloses show comparatively good resistance, of the same order as secondary cellulose acetate.

Fibres of cyanoethyl cellulose spun from acetone solution possess a more subdued lustre than acetate rayon fibres and have a silkier handle. They show a good affinity for acetate dyes, but the tendency is for dyeings to be flatter on cyanoethyl than on acetate yarn. Basic dyes, applied without a

mordant, give solid bright shades. Direct cotton dyes have a poor affinity.

Reaction of Acrylonitrile with Starch

Starch with its three free hydroxyl groups per anhydroglucose unit reacts with acrylonitrile in the same manner as cellulose, forming cyanoethyl ethers. Fig. 3 shows that the reaction between

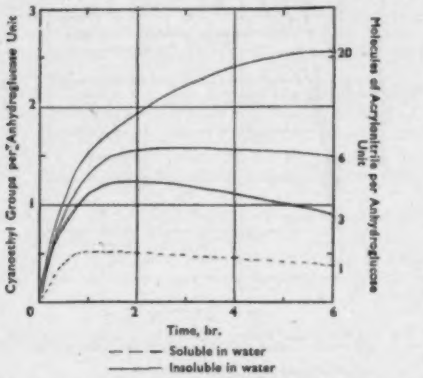


FIG. 3—Reaction of Varying Proportions of Acrylonitrile with Starch at 30°C. (3 NaOH per anhydroglucose unit)

starch solutions and acrylonitrile, catalysed by sodium hydroxide, follows much the same course as does the reaction between viscose and acrylonitrile. The starch–acrylonitrile reaction proceeds more rapidly and a greater degree of substitution is obtained for corresponding quantities of acrylonitrile. The products are, however, different in character from those obtained from cellulose. They fall into the same three groups, viz. water-soluble, water-insoluble (caustic alkali-soluble), and solvent-soluble ethers.

(*a*) WATER-SOLUBLE ETHERS

Water-soluble cyanoethyl starch ethers are obtained when the molar ratio of acrylonitrile to glucose units in starch is 0·1–1·5. It is found that the maximum introduction of cyanoethyl groups occurs when the molar ratio of sodium hydroxide to starch is 1 : 1. Neutralization of the reaction mixture gives thick sticky solutions, which are freed from electrolytes by dialysis. The dry ethers are obtained from their solutions by precipitation with ethanol or acetone. When dried at 100°c. the ethers are crisp, white solids, which readily swell and dissolve in water to give colourless transparent solutions. When the molar ratio of acrylonitrile to starch is $> 0{\cdot}5$ the ethers obtained give no coloration with the usual iodine reagent for starch. The water-soluble cyanoethyl starch ethers possess good emulsifying and dispersing properties. They have also proved themselves to be good sizes for textile yarns.

(*b*) WATER-INSOLUBLE, ALKALI-SOLUBLE ETHERS

Ethers of this class are obtained when the molar ratio of acrylonitrile to starch is > 2 and when the reaction is carried out in aqueous solutions of sodium hydroxide. The ethers obtained on neutralizing the reaction mixture swell considerably in water but do not dissolve. They are soluble in dilute aqueous sodium hydroxide solutions, and when the degree of substitution rises above 2 cyanoethyl groups per anhydroglucose unit they swell and dissolve in aqueous acetone. These ethers can be used for the application of pigments to fabrics by the padding process and as permanent finishing agents for textile fabrics.

(*c*) SOLVENT-SOLUBLE ETHERS

It has been shown[16] that solvent-soluble cyanoethyl starch ethers are not prepared by the direct reaction of swollen starch with acrylonitrile in the presence of a strong alkaline condensing agent. They are, however, readily prepared by treating a low-substituted cyanoethyl starch ether with an excess of acrylonitrile in the presence of a small amount of aqueous sodium hydroxide. The reaction is best carried out at the refluxing temperature of the acrylonitrile (77–78°c.). The cyanoethyl starch ethers obtained contain 2·5–3·0 cyanoethyl groups per anhydroglucose unit and are soluble in such solvents as acetone, dimethylformamide, and γ-valerolactone. The experimental conditions under which these solvent-soluble ethers are prepared from low-substituted cyanoethyl starch ethers are similar to those under which solvent-soluble cyanoethyl cellulose ethers are prepared from partial cyanoethyl cellulose ethers[33].

As would be expected, amylose, the straight-chain component of starch, and amylopectin, the branched-chain component, react with acrylonitrile in the presence of aqueous sodium hydroxide in a similar manner to starch, to give water-soluble, water-insoluble (caustic alkali-soluble), and solvent-soluble cyanoethyl ethers.

Reaction of Acrylonitrile with Polyvinyl Alcohol

Polyvinyl alcohol dissolves in water to give viscous solutions and is a typical hydrosol. It is the only known form of the hypothetical vinyl alcohol $CH_2{:}CH{\cdot}OH$. Staudinger[34], who prepared polyvinyl alcohol by hydrolysis of polyvinyl acetate, ascribed to it a 1:3-glycol structure—

$$[CH_2{\cdot}CH(OH){\cdot}CH_2{\cdot}CH(OH)]_n$$

This structure has been confirmed by the work of Herrmann and Haehnel[35] and by that of Marvel and Denoon[36]. The former workers showed that polyvinyl alcohol could be prepared by either alkaline or acid hydrolysis of polyvinyl acetate. Alkaline hydrolysis tends to yield polyvinyl alcohols which are yellow or brown in colour, whereas acid hydrolysis gives colourless products. Commercial varieties of polyvinyl alcohol contain varying amounts of unsaponified polyvinyl acetate. The polyvinyl alcohol used in the experiments described in this paper contained slightly less than 2·5% unsaponified ester units.

Staudinger[37] in his classical researches on the nature of macromolecules has used successfully a number of synthetic substances as representatives of certain specific groups of natural products.

Thus, the polyoxymethylenes were used as a model for cellulose, while polyvinyl alcohol and polyvinyl acetate were selected as models for starch and esters of polysaccharides respectively.

As might be expected from the similar colloidal behaviour of polyvinyl alcohol and starch, the reaction between acrylonitrile and polyvinyl alcohol solutions in the presence of strong alkaline condensing agents follows a similar course to that between acrylonitrile and starch. Thus, water-soluble cyanoethyl ethers are formed initially, and as cyanoethylation proceeds the products of the reaction become more and more insoluble in water. This latter group of partial ethers shows an increasing tendency to swell in aqueous sodium hydroxide as well as in aqueous ethanol and aqueous acetone.

Table I shows how the nitrogen content of the cyanoethylated polyvinyl alcohol increases as the molar proportion of acrylonitrile is raised. In this series of experiments a 5% aqueous polyvinyl alcohol solution was used and the molar ratio of polyvinyl alcohol to sodium hydroxide was 1 : 1. The reactions were performed in flasks which were agitated mechanically in a waterbath thermostatically controlled at 20°C. The reaction time was 3 hr.

TABLE I

Moles of Acrylonitrile per Monomer Unit of Polyvinyl Alcohol	Nitrogen Content (% of dry ash-free sample)	Cyanoethyl Groups per Monomer Unit of Polyvinyl Alcohol	Solubility of Reaction Product in Water
0·1	0·9	0·029	Soluble
0·2	1·8	0·061	Soluble
0·3	2·6	0·095	Soluble
0·4	3·6	0·131	Soluble
0·5	4·8	0·184	Soluble
0·6	5·1	0·198	Soluble
0·75	5·6	0·223	Soluble
1·0	6·6	0·277	Soluble
1·5	8·3	0·380	Semi-soluble
2·0	8·7	0·408	Semi-soluble
2·5	9·0	0·429	Semi-soluble
3·0	9·1	0·436	Insoluble
3·5	9·1	0·436	Insoluble
4·0	9·7	0·482	Insoluble
4·5	10·0	0·506	Insoluble

From Table I it is seen that when less than 0·3 cyanoethyl group is present per monomer unit the products are water-soluble. At degrees of substitution higher than this the products are water-insoluble. Fig. 4 indicates the course of the reaction rates when greater molar proportions of acrylonitrile are used.

Cyanoethyl ethers of polyvinyl alcohol soluble in solvents such as acetone cannot be prepared direct from aqueous solutions of the polyvinyl alcohols. They are prepared by treating polyvinyl alcohol or a partial cyanoethyl ether with excess of acrylonitrile in the presence of a small amount of aqueous sodium hydroxide at about 80°C. (cf. Houtz[28]). These ethers contain 0·8–1·0 cyanoethyl group per monomer unit. They dissolve as they form in the excess of acrylonitrile present, and may be isolated by pouring the reaction mixture into 50% aqueous ethanol. The precipitated ether is then acidified,

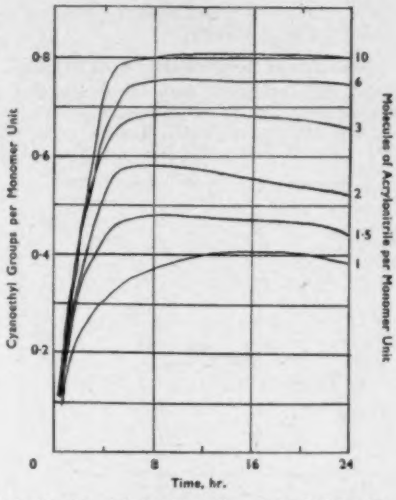


FIG. 4— Reaction of Various Proportions of Acrylonitrile with Polyvinyl Alcohol at 20°C. (1 NaOH per monomer unit)

washed free from acid with water, and finally dried over phosphorus pentoxide *in vacuo*. Films of these ethers cast from their acetone solutions are plastic and sticky. They possess good adhesive properties.

Solutions of the water-soluble cyanoethyl ethers of polyvinyl alcohol, on the other hand, deposit tough, pliable, transparent films on evaporation. These aqueous solutions can be used for sizing textile yarns.

Theory of the Reaction

It has been mentioned already when discussing the interaction between acrylonitrile and viscose that the reaction is not simply a matter of addition. This is also true of the reaction of acrylonitrile with starch and with polyvinyl alcohol. If it were simply additive, it would proceed until equilibrium had been reached and then cease. As the curves show, this is not the case. In both cases the nitrogen content reaches a maximum and then falls. This is due, of course, to the hydrolysis of cyanoethyl groups to carbamylethyl and then to carboxyethyl groups. In the graphs it has been assumed that the nitrogen is present entirely as nitrile groups. This is not a true picture, but the method has been used since it gives a useful guide to the progress of cyanoethylation, especially in the early stages.

Infra-red analysis has shown that the moderately cyanoethylated ethers such as certain water-soluble celluloses and water-insoluble starch and polyvinyl alcohol ethers do contain carbamyl groups and in some instances carboxy groups. Actually, from these infra-red examinations there are indications that not more than 10% of the cyano groups had been hydrolysed to carbamyl groups[17]. The majority of the low-substituted cyanoethyl ethers examined in the infra-red showed no evidence of the presence of carbamylethyl groups: only cyanoethyl groups were detected. This is true also of

all the acetone-soluble cyanoethyl ethers, i.e. the highly or completely cyanoethylated substances.

As the reaction is catalysed by strong alkaline condensing agents, it is to be expected that the acrylonitrile also is hydrolysed according to a similar scheme—

$$CH_2{:}CH{\cdot}CN + H_2O \rightarrow CH_2{:}CH{\cdot}CO{\cdot}NH_2 \quad (i)$$

$$CH_2{:}CH{\cdot}CO{\cdot}NH_2 + NaOH \rightarrow CH_2{:}CH{\cdot}COONa + NH_3 \quad (ii)$$

Evidence of this can be found in the fact that more acrylonitrile is used than is accounted for by the total substituted groups in the macromolecular substance.

It can be assumed that the acrylamide and the sodium acrylate, even if they react at all, will have a very much lower rate of condensation with the polymeric substance than the nitrile, so that, in effect, this hydrolysed material is lost to the main reaction.

Furthermore, it has been found that water adds to acrylonitrile in the presence of an alkaline catalyst to give ethylene cyanohydrin, which reacts still further with acrylonitrile, yielding bis-2-cyanoethyl ether[39]—

$$CH_2{:}CH{\cdot}CN + H_2O \rightarrow HO{\cdot}CH_2{\cdot}CH_2{\cdot}CN \quad (a)$$

$$CN{\cdot}CH{:}CH_2 + HO{\cdot}CH_2{\cdot}CH_2{\cdot}CN \rightarrow CN{\cdot}CH_2{\cdot}CH_2{\cdot}O{\cdot}CH_2{\cdot}CH_2{\cdot}CN \quad (b)$$

The presence of these substances in the reaction mixture has been confirmed, and accounts for part at least of the acrylonitrile lost to the main reaction.

Hydrolysis of Cyanoethyl Ethers

It has been shown[10] that β-alkoxypropionitriles when hydrolysed with boiling aqueous 5% sodium hydroxide or concentrated hydrochloric acid yield the corresponding β-alkoxypropionic acids—

$$R{\cdot}O{\cdot}CH_2{\cdot}CH_2{\cdot}CN \xrightarrow{H_2O} R{\cdot}O{\cdot}CH_2{\cdot}CH_2{\cdot}CO{\cdot}NH_2$$

$$\xrightarrow{NaOH} R{\cdot}O{\cdot}CH_2{\cdot}CH_2{\cdot}COONa + NH_3$$

$$R{\cdot}O{\cdot}CH_2{\cdot}CH_2{\cdot}CN \xrightarrow[+2H_2O]{HCl} R{\cdot}O{\cdot}CH_2{\cdot}CH_2{\cdot}COOH + NH_4Cl$$

Hydrolysis with boiling aqueous sodium hydroxide (5–10% NaOH) of the cyanoethyl ethers described in this paper gives the carboxyethyl ethers, but there is evidence that fission at the ether linkage also occurs with re-formation of the original hydroxy substance. It was noted, for example, that when triscyanoethyl cellulose was boiled with 5% aqueous sodium hydroxide, ammonia was liberated. Complete removal of the ammonia showed that, while the cellulosic products of hydrolysis contained no nitrogen, the carboxy groups present in the products accounted for only one-quarter of the nitrogen liberated as ammonia. Further examination of the reaction mixture showed the presence of β-hydroxypropionic acid, which was identified as β-iodopropionic acid (m.p. 82°C.; no depression of melting point on admixture with an authentic specimen). The isolation of this acid from the products of hydrolysis indicated that fission had occurred at the ether linkage.

From these results it would seem that the interaction of boiling aqueous sodium hydroxide solutions with the cyanoethyl ethers described in this paper results in fission at the ether linkage and normal nitrile hydrolysis—

$$R{\cdot}O{\cdot}CH_2{\cdot}CH_2{\cdot}CN \xrightarrow{H_2O} R{\cdot}O{\cdot}CH_2{\cdot}CH_2{\cdot}CO{\cdot}NH_2$$

$$R{\cdot}O{\cdot}CH_2{\cdot}CH_2{\cdot}CO{\cdot}NH_2 \xrightarrow{H_2O} R{\cdot}O{\cdot}CH_2{\cdot}CH_2{\cdot}COOH + NH_3$$

$$R{\cdot}O{\cdot}CH_2{\cdot}CH_2{\cdot}CN \longrightarrow R{\cdot}OH + CH_2{:}CH{\cdot}CN$$

$$\downarrow H_2O$$

$$HO{\cdot}CH_2{\cdot}CH_2{\cdot}COOH \xleftarrow{H_2O} HO{\cdot}CH_2{\cdot}CH_2{\cdot}CN$$

Indeed, a recent comprehensive study[30] of the hydrolysis of β-alkoxy- and β-aryloxy-propionitriles with boiling aqueous sodium hydroxide solution strongly indicates that considerable fission occurs at the ether linkage, yielding the alcohols.

The author wishes to thank the Directors of Messrs. Courtaulds Ltd. for permission to publish the results of this investigation.

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The Reaction of Acrylonitrile with Macromolecular Hydroxy Substances
II—The Production and Uses of Water-insoluble, Alkali-soluble Cyanoethyl Cellulose Ethers as Soluble Yarns

J. H. MacGregor and C. Pugh

The conditions under which viscose and acrylonitrile react so that cyanoethyl cellulose yarns, which are insoluble in water but soluble in cold weak aqueous solutions of the caustic alkalis and quaternary ammonium hydroxides, can be spun, are outlined; the chemistry of the complex reaction is fully discussed. The usefulness of these cyanoethyl cellulose yarns as soluble reinforcing threads for twistless cotton fabrics and as substitutes for the draw-thread in the continuous production of children's half and quarter hose composed of cotton and/or viscose rayon yarns is considered. Finally, a very brief account is given of the dyeing of these yarns with direct cotton dyes.

Introduction

The preparation of cyanoethyl ethers of cellulose, soluble in a range of solvents including water, weak aqueous caustic alkalis, and acetone, has been discussed in the previous paper of this series[1] (p. 66). In this paper the production and application as soluble yarns of cyanoethyl celluloses, insoluble in water but soluble in weak aqueous solutions of caustic alkalis, will be considered.

Soluble yarns have two main uses—in the production of fabrics containing yarn of little or no twist and as a substitute for the draw-thread in hose manufacture.

In the former use they are doubled with a twisted staple yarn, the doubling twist being in the opposite direction and equal to that of the staple yarn (e.g. a singles staple yarn of "S" twist, 20 turns, is doubled with a soluble yarn of "Z" twist, 20 turns). Unlike twistless staple yarns, these doubled yarns knit and weave well. When the fabric is constructed, the soluble yarn is removed by dissolution in a suitable solvent, leaving the staple yarns with zero twist. Soluble yarns which have been used in this way include cellulose acetate rayon and calcium alginate rayon.

Various possible applications of twistless fabrics have been listed by Johnson and Speakman[2]—for example, twistless cotton fabrics have been used as filter cloths, in the manufacture of rainproof fabrics, and for the reinforcement of plastic laminates.

In the second application the soluble yarns replace the draw-thread used in the continuous manufacture[3] of quarter and half hose to prevent a ragged edge or fringe where the socks are separated.

The main requirements of a soluble yarn are—

(1) Solubility in a cheap solvent which will leave the majority of other textile fibres unaffected

(2) Good appearance and strength

(3) Simple and inexpensive production.

While the water-insoluble, alkali-soluble cyanoethyl celluloses, unlike calcium alginate rayon, are not soluble in mild scouring agents containing such mild alkalis as sodium carbonate, they are very readily soluble in cold weak aqueous solutions of the caustic alkalis, like sodium hydroxide, and the quaternary ammonium hydroxides, such as trimethylbenzylammonium hydroxide (Triton B). Thus, a low-substituted, water-insoluble cyanoethyl cellulose can be prepared easily which will dissolve quickly in a cold 1–2% aqueous solution of sodium hydroxide. These solutions are unsatisfactory where it is desired to remove a "soluble yarn" and leave a fibrous protein yarn such as wool unaffected, but where the yarns to be left undamaged consist entirely of native or regenerated cellulose the use of such solutions is entirely satisfactory. To remove water-insoluble cyanoethyl cellulose yarns satisfactorily in the presence of fibrous proteins a cold 25% aqueous solution of ammonium thiocyanate may be used. This readily dissolves the cyanoethyl cellulose yarns, leaving the fibrous protein yarns undamaged. It is clear, therefore, that this group of low-substituted cyanoethyl cellulose yarns (referred to subsequently in this paper as CECC yarns, the final C denoting solubility in caustic alkalis) fulfil, in part at least, the first requirement listed above of a soluble yarn.

By reaction of acrylonitrile with viscose, CECC yarns can be produced having a dry tenacity of 1·5 g. per denier, which is satisfactory for a "carrier" thread. While the quality of such yarns is lower than that of viscose rayon yarns, they can be produced with a satisfactory handle and appearance and thus fulfil our second requirement.

The third requirement can be easily met, since these CECC yarns can be produced in a plant and with machinery similar to those in use for the production of viscose rayon yarn. No special adaptation of the plant is necessary, the sole additional requirement being the strict control of working temperature: the spinning solution has to be maintained at 15°C.

Experience has shown that there is no grade of cyanoethyl cellulose ethers which is soluble in sodium carbonate and not in water, at an intermediate stage between grades soluble in water and those soluble in sodium hydroxide. The limit to the degree of substitution at which spinning ceases to be practicable appears to be about 0·25 cyanoethyl group per anhydroglucose unit. At higher degrees of substitution the yarn can be spun, but it is so swollen and weak in the washing and drying stages that damage due to handling is inevitable. It is, however, possible to spin and process a yarn which is dissolved by a 0·8% aqueous sodium hydroxide solution at 20°C., and this has satisfactory strength, appearance, and handle. The extensibility of these yarns is high, being of the order of 25% at the break for dry yarn.

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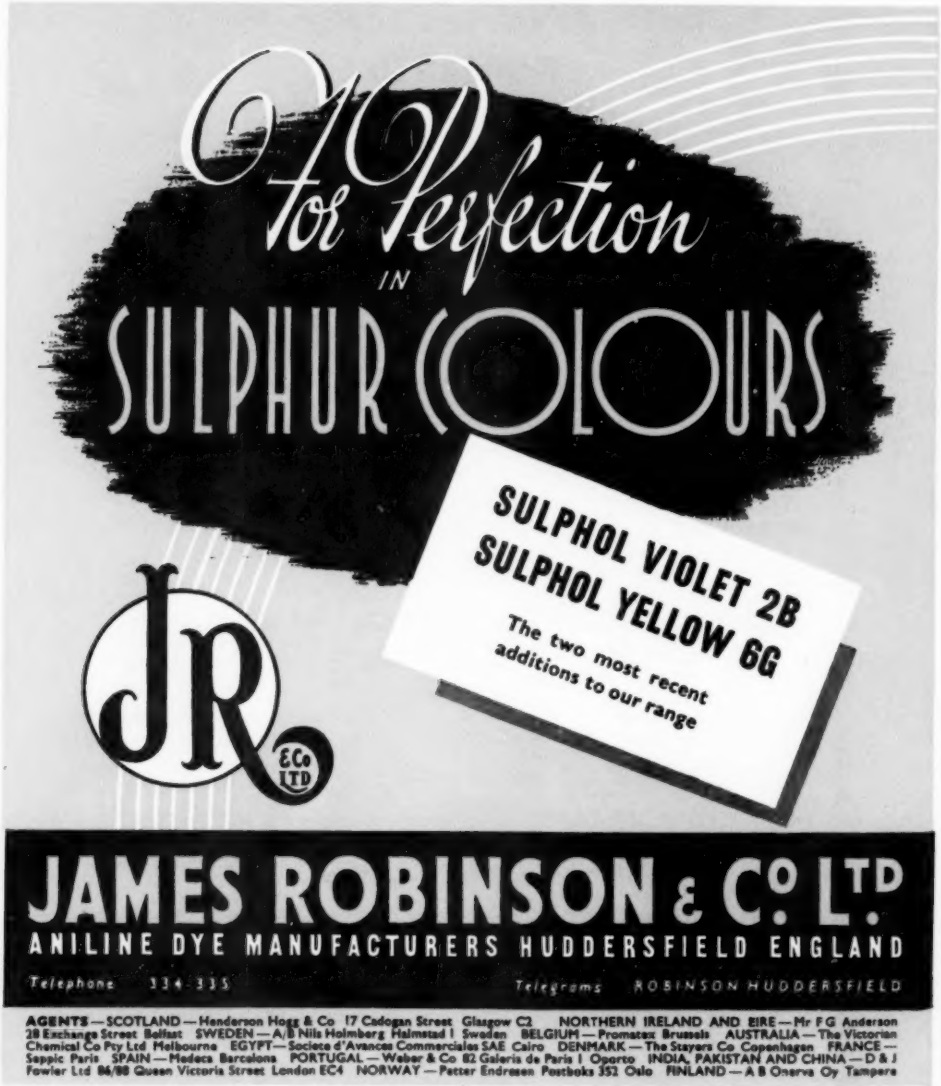
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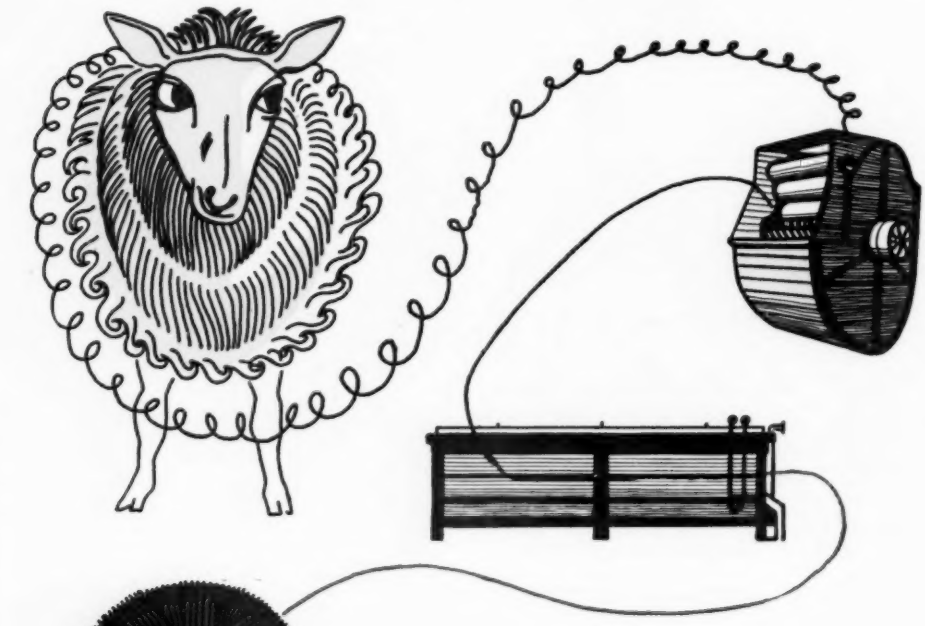

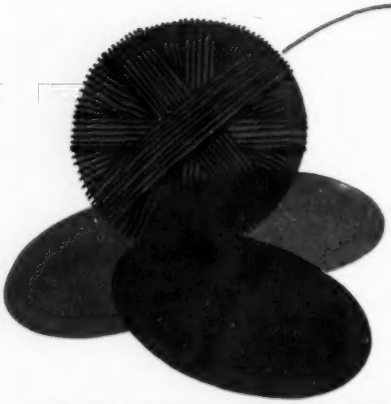

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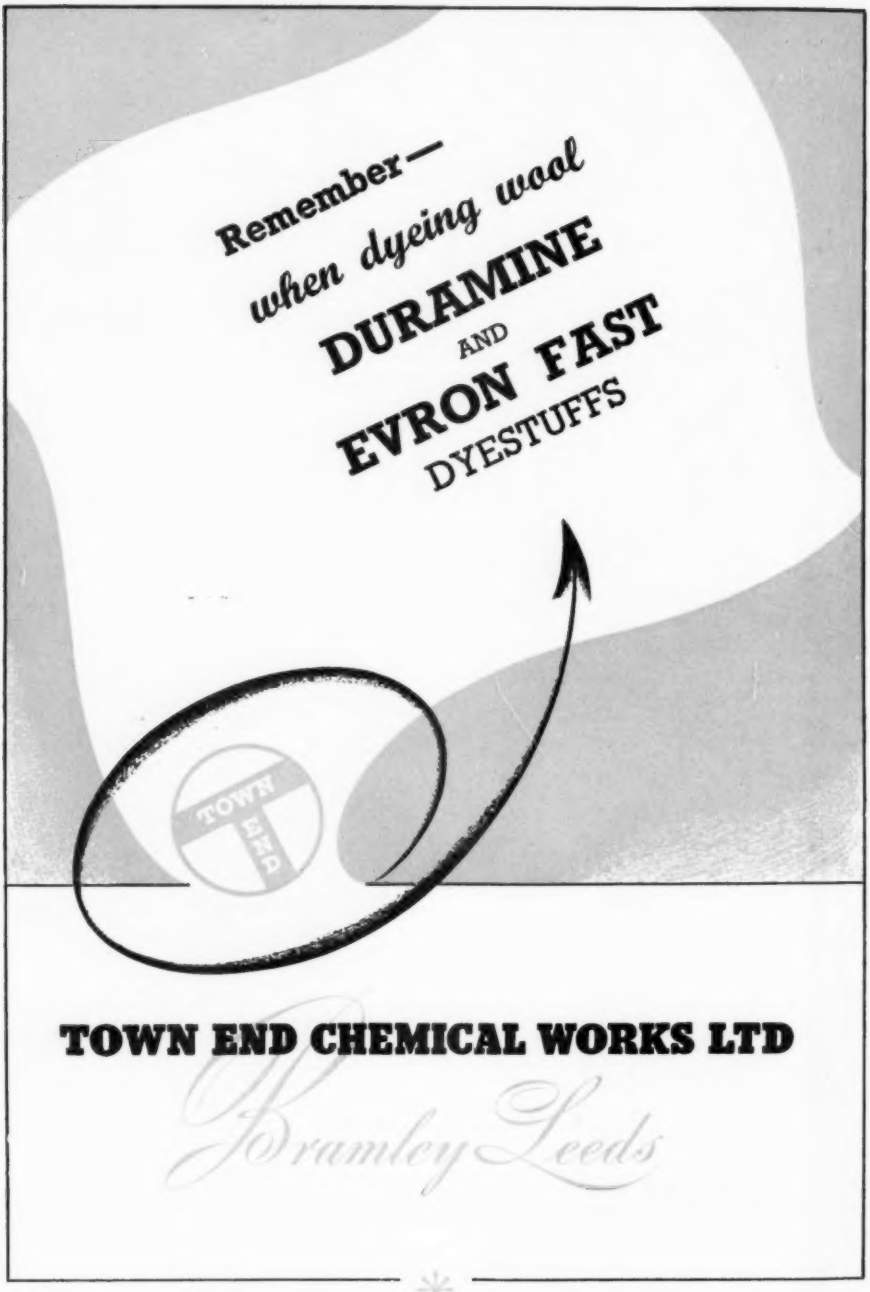
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The Reaction of Acrylonitrile with Viscose

The reaction between acrylonitrile and viscose is extremely complex and is further obscured by two prominent side-reactions, one with the by-products of ageing and the other with water catalysed by alkalis. These side-reactions waste acrylonitrile and are undesirable in a process for the production of a yarn. Most of the critical factors can now be controlled satisfactorily albeit empirically. The following are the three main variables affecting the rate of reaction and physical properties of the yarn produced—

1. AGE OF THE VISCOSE TREATED WITH ACRYLONITRILE

This has a dual effect on the spinning. It is well known that the degree of ripening normally affects the spinning of ordinary viscose rayon yarn, and this condition also affects the spinning of CECC yarn. The proportion of by-products, such as sodium trithiocarbonate and sodium sulphide, also depends on the age of the viscose. These react with acrylonitrile to form bis-β-cyanoethyl sulphide ($\beta\beta'$-thiodipropionitrile)[4], reducing the amount of acrylonitrile available for cyanoethylation. The degree of substitution is not greatly affected by age of the viscose, but the solubility in cold weak aqueous caustic soda solutions is altered appreciably.

After preliminary experiments, it appeared that the optimum salt index was 5·5; all the preparations described in this paper were made with viscose of this degree of ripeness.

2. AGE OF THE SOLUTION AFTER REACTING WITH ACRYLONITRILE

The reaction is dependent on time and temperature, and unless both are strictly controlled the production of uniform yarn becomes difficult. The reaction between acrylonitrile and viscose proceeds in several steps, outlined in Fig. 1. At first there is the simple addition of acrylonitrile to a hydroxyl group, catalysed by alkali. The resulting cyanoethyl cellulose xanthate can then age in the normal way, and the cyano group will gradually hydrolyse to a carboxy group.

The carboxyethyl cellulose itself appears to undergo a further reaction, as for every nitrile group hydrolysed only between one-quarter and one-third of a carboxy group is found by analysis. This observation appears to be explained by the hydrolysis of the carboxyethyl cellulose back to cellulose and the formation of β-hydroxypropionic acid, as already shown by MacGregor[1].

In Fig. 2 the reaction curves for equimolar quantities of acrylonitrile and viscose at several temperatures are plotted. At 25°C. the number of nitrile groups per anhydroglucose unit reaches a maximum in 2–3 hr., and falls off sharply after about 5 hr. as hydrolysis of the nitrile group becomes the prominent reaction. At 20°C. the hydrolysis takes longer to gain effect, and then the

FIG. 1.—Main and Side Reactions between Viscose and Acrylonitrile

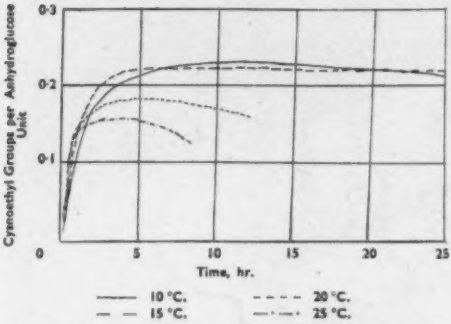

FIG. 2—Reaction of Viscose with Acrylonitrile (1 molecule per anhydroglucose unit) at Various Temperatures

rate of hydrolysis is lower. At 15°C. and 10°C. the effect of hydrolysis has not become appreciable even after some 20 hr. The temperature below which it is necessary to work in order that the degree of substitution shall remain constant over the period of 8 to 20 hr. after mixing, that is required for spinning, is in the neighbourhood of 16°C. Reducing the reaction temperature below this point slows down the rate of the addition reaction without any gain in reduction of the rate of the hydrolysis. Thus, by careful control of the time and temperature, uniform yarn may easily be spun on a batch-preparation basis.

An experiment has been performed in which the ageing of the CECC solution has been carried to extreme length to determine the properties of the yarn produced. Work on similar lines has been reported by Hollihan and Moss[5]. The reaction was carried out at room temperature, and batches of yarn were spun and processed at intervals of 12 hr. over a period of 90 hr.

The nitrogen content of the yarns was determined by the Kjeldahl method and was expressed as cyanoethyl groups, although in fact this gave the total of both cyanoethyl and carbamylethyl groups per anhydroglucose unit. The number of carboxyethyl groups was obtained by soaking the yarns in cold 2 N. hydrochloric acid for 30 min., removing, rinsing in cold distilled water, transferring to an electrodialyser, and dialysing to remove completely all cations. The yarns were then placed

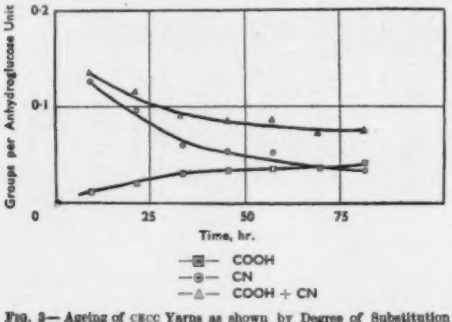

FIG. 3—Ageing of CECC Yarns as shown by Degree of Substitution with Cyano and Carboxyl Groups

in flasks and titrated with 0·02 N. sodium hydroxide (cf. Neale and Stringfellow[6]). The results are shown graphically in Fig. 3.

It is clear that carboxyl groups do not appear as rapidly as nitrile and carbamyl groups are lost, as indicated by the reduction in nitrogen content. This, of course, is accounted for by the further hydrolysis of the carboxyethyl group to give cellulose, as mentioned earlier in this paper (p. 75). The rate of this further hydrolysis of carboxyethyl groups is comparable with that of the formation of carboxyl groups.

It will also be seen that, as the spinning solution ages, the CECC yarn produced from it requires stronger solutions of aqueous sodium hydroxide to effect its dissolution (Fig. 4). This is probably connected with the decrease in total cyano plus carboxyl groups as the solution ages.

3. PROPORTION OF ACRYLONITRILE USED

The degree of substitution of the final yarn depends on the molar ratio of the reactants and is modified only by the conditions of time and temperature employed for the reaction. Fig. 5 gives the relationship between the molar ratio of acrylo-

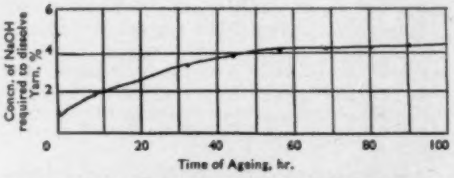

FIG. 4—Effect of Ageing of CECC Yarns on their Solubility in Caustic Soda

nitrile to viscose employed and the degree of substitution attained under optimum conditions at 15°C. It will be seen that the curve rises roughly linearly up to a ratio of 4 moles of acrylonitrile per molar anhydroglucose unit of cellulose, and then begins to flatten out. The linear part of the curve can be expressed approximately by the formula—

$$\text{Degree of substitution} = 0{\cdot}34 \times (\text{molar ratio} - 0{\cdot}5)$$

This means that 0·5 mole of acrylonitrile is consumed in side-reactions, presumably with sodium trithiocarbonate and with sodium sulphide; and that rather less than half the remaining acrylonitrile is consumed by reaction with sodium cellulose xanthate. The remaining acrylonitrile must be used up in reaction with the water, forming ethylene cyanohydrin, whose presence in the reaction mixture has been confirmed as also has that of small amounts of bis-2-cyanoethyl ether. This latter substance appears to be formed by reaction of acrylonitrile with ethylene cyanohydrin (cf. Bruson and Riener[7]). This series of reactions can be expressed by the following equations—

$$CH_2{:}CH{\cdot}CN + H_2O \rightarrow HO{\cdot}CH_2{\cdot}CH_2{\cdot}CN \quad (a)$$

$$CN{\cdot}CH{:}CH_2 + HO{\cdot}CH_2{\cdot}CH_2{\cdot}CN \rightarrow CN{\cdot}CH_2{\cdot}CH_2{\cdot}O{\cdot}CH_2{\cdot}CH_2{\cdot}CN \quad (b)$$

As the degree of substitution is increased by reaction with increasing quantities of acrylonitrile, the properties of the ethers undergo a gradual

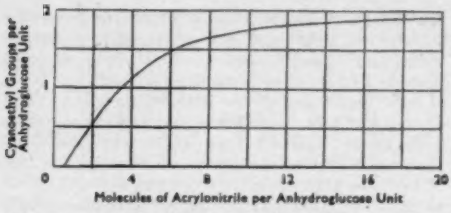

FIG. 6.—Effect of Proportion of Acrylonitrile on Maximum Degree of Substitution of Viscose

change. They gradually increase in alkali-solubility up to about 1·5 moles of acrylonitrile per molar anhydroglucose unit in cellulose, when a water-soluble range is reached. Above 4·0 moles of acrylonitrile, again, the ethers become increasingly less soluble in caustic alkalis.

For production of soluble fibres we are concerned only with the molar range from 0·9 to 1·1. Below this range the strength of sodium hydroxide required for solution is excessive; above it the yarn is extremely difficult to process without damage. Table I gives some data in this range.

TABLE I

Physical Properties of CECC Yarns

Molecules of Acrylonitrile (per anhydroglucose unit)	Cyanoethyl Groups	Tenacity (g./denier)		Extension (%)		Concentration of NaOH (%) for	
		Dry	Wet	Dry	Wet	Swelling	Soln.
1·10	0·27	1·52	0·32	26·1	78·3	0·8	1·0
1·05	0·26	1·66	0·39	25·0	74·1	1·0	1·1
1·00	0·21	1·74	0·45	23·0	60·0	1·0	1·25

The ratio of acrylonitrile used determines the degree of substitution and the solubility of the yarn attainable. The control of temperature and reaction time ensures that this degree of substitution is reached and remains constant throughout the duration of spinning.

The spinning bath is an acid–salt mixture; the following has been found to be suitable—

9·5%	...	Sulphuric acid
16·0%	...	Sodium sulphate
10·0%	...	Magnesium sulphate
1·0%	...	Zinc sulphate

One of the major problems in the production of CECC yarn is the formation of $\beta\beta'$-thiodipropionitrile, by reaction of acrylonitrile with the by-products, such as sodium trithiocarbonate and sodium sulphide, formed during the ageing of the viscose, as was shown earlier in this paper (cf. also MacGregor and Pugh[4]). The formation of this substance was forecast by Hollihan and Moss[5], but it was not isolated nor was its structure confirmed by these authors. When CECC yarns were first prepared and spun at room temperatures, considerable trouble was experienced with dirty jets and clogged filter candles. When the reaction conditions were controlled at 15°C., the dirty jet trouble was reduced, but filter candles very rapidly became caked with a yellow, finely crystalline precipitate. Analysis showed this to be $\beta\beta'$-thiodipropionitrile. The oily dispersion first formed crystallized at 15°C. and was retained by the filters. If the reaction mixture was not cooled, fine droplets of the substance passed through the filters and broke the filament continuity at jet holes, causing dirty jets to develop.

It was found most convenient to insert a filtration stage between mixing and vacuum treatment of the solution, as well as a small-scale line filtration immediately before the spinning machine to remove the small quantity formed during vacuum treatment by ageing of the cyanoethyl cellulose xanthate. When this was done the trouble was eliminated and no further difficulty was experienced with the spinning.

Processing the Yarn

CECC yarn, on account of its high degree of swelling, is readily washed free of acid. The resultant yarn is in a highly plastic condition and has to be handled with great care to avoid damage. If it is centrifuged and dried without further treatment very harsh yarn with excessive filament sticking results.

In order to overcome this sticking together of filaments, the effects of a series of softening agents of diverse types were investigated as treatments for the yarn prior to drying. In general, cationic paraffin-chain salts were found to be more beneficial than those of an anionic character, the former being characterized by a high degree of substantivity for textile fibres. Thus treatment of CECC yarn in a 0·1% aqueous solution of laurylpyridinium bromide, followed by centrifuging and drying, gives a yarn possessing a good handle and appearance, free from any sign of adhering filaments.

Solubility of CECC Yarn

The solubility of CECC yarn has been measured in terms of the strength of the solution of sodium hydroxide that will dissolve the yarn completely on shaking for 5 min. It has been found that this method gives results reproducible for 0·1% change in strength of solution. To perform the test a specimen of the yarn is wetted by soaking in distilled water for about 10 min., and freed from excess moisture by squeezing in a cloth; small portions are then shaken for 5 min. with 10-c.c. quantities of sodium hydroxide solutions of varying strengths. Three values within a range of 0·2% of solution strength may be found for which the yarn becomes highly swollen, then dispersed, and finally completely dissolved, respectively.

The solubility depends largely on two factors—the proportion of cyanoethyl groups introduced into the cellulose molecule and the proportion of these groups hydrolysed by sodium hydroxide present in the solution before the yarn is spun. These factors are functions of the ratio of acrylonitrile to cellulose used and the age of the spinning solution at the jet. No test analogous to the salt index or ammonium chloride ripeness tests used for determining the age of viscose has been evolved for CECC solutions, so that the chemical age is regulated by strict control of the times and temperatures employed.

The nitrogen content of CECC yarn gives a measure of the degree of cyanoethylation but does not correlate fully with the solubility of the yarn. It has been shown by infra-red spectrographic examination of samples of CECC prepared from differing molar proportions of acrylonitrile and cellulose that the distribution of nitrile groups within the molecule is a function of the proportions employed, and that the solubility is correlated with this distribution. It is a function also of the age of the spinning solution, in that the character of the cyanoethyl groups introduced is changed by hydrolysis (cf. Fig. 1), and this change in chemical constitution affects the solubility. It has been found that, if two samples of CECC are prepared from different molar ratios of acrylonitrile to cellulose but have the same nitrogen content (by control of time and temperature of reaction), their solubility is directly related to the ratio of reactants used.

When acrylonitrile adds to a hydroxy group in the cellulose molecule, that molecule and the adjacent one are pushed apart to admit the larger bulk of the cyanoethyl group. This causes strain and disruption of the adjacent hydrogen bonds, and if sufficient cyanoethyl groups are introduced the chains are dispersed sufficiently to free enough hydroxy groups to confer solubility in water on the cellulose derivative. Indeed, the X-ray diagram of CECC fibres closely resembles that of fibres of mercerized cellulose (cf. Happey and MacGregor[9]). It also shows that the crystallites are badly defined, owing to the considerable lattice distortion caused by the substitution in the cellulose molecule of some of the hydroxy groups by cyanoethyl groups. When CECC fibres are allowed to swell in water, a large increase in diameter of the fibres is observed, but sufficient of the crystal lattice is retained to prevent the fibre from going into solution. When, however, a 1·25% aqueous solution of sodium hydroxide is used to swell the yarn, the whole crystal lattice appears to be penetrated, and the ether consequently goes completely into solution. If the nitrile groups are hydrolysed to carboxy groups and these latter react further, as suggested above, re-formation of the cellulose may occur with subsequent cross-linking of the chains, which will account for the decrease in solubility of yarns spun from very old solutions.

Production and Application of CECC Yarn on a Semi-large Scale

The foregoing points are best illustrated by a description of the semi-large scale production[10] of about 2·25 kg. of 100-denier/36-filament CECC yarn. This yarn was subsequently used as a substitute for the draw-thread in the production of a quantity of children's viscose rayon–cotton socks by a continuous knitting process. Details are also given for the complete removal of the CECC threads from the socks.

Viscose (30 kg.) containing 7·75% by weight of cellulose (14·35 moles of anhydroglucose) and 6·2% by weight of sodium hydroxide and having a salt index of 5·5 was cooled to 10°C. and mixed in an enamelled pot with 950·6 c.c. of acrylonitrile (14·35 moles). The reaction mixture was stirred for 90 min. at 10°C., and the $\beta\beta'$-thiodipropionitrile which had separated out was filtered through one plate of a 12-in. filter press wrapped with one layer of swansdown and a fine calico filter cloth. The area of the press was 300 sq. in. and the pressure 40 lb./sq. in. Filtration was complete in about 1 hr. The temperature of the filtrate was then 13°C. The filtrate was kept under reduced pressure (25 in. of mercury) for 5 hr. with the temperature maintained at 15°C., and then extruded in a similar manner to viscose through a jet having sixty 3-mil holes, into the coagulating bath at 40°C. whose composition has been given on p. 77.

Spinning was continued for 8 hr., and during this time the temperature of the spinning solution was maintained at 15°C. The cakes of CECC yarn obtained were reeled into skeins and washed free from acid with water. The acid-free skeins were finally treated for 30 min. in a 0·1% aqueous solution of laurylpyridinium bromide, centrifuged, and air-dried at 40°C.

The CECC yarn thus obtained had the following properties—

Denier	100
Water imbibition	265%
Tenacity (dry)	1·75 g./denier
Tenacity (wet)	0·45 g./denier
Extensibility (dry)	23·0%
Extensibility (wet)	60·0%
Concn. of aq. NaOH to swell yarn	1·1%
Concn. of aq. NaOH to dissolve yarn	1·25%
Nitrile N content of yarn	1·73%
No. of cyanoethyl groups per anhydroglucose unit	0·215

The CECC yarn was then four-folded, and used as a substitute for the draw-thread in the production of a supply of children's quarter hose knitted by a continuous process from yarns composed of a 2-fold cotton yarn plaited with a viscose rayon yarn. No difficulty was experienced with the CECC yarns in the knitting process.

The removal of the CECC draw-thread was investigated. It was noted that, while it was comparatively simple, by treatment of the socks with dilute aqueous solutions of sodium hydroxide, to remove the CECC yarns without impairing the constituent yarns of the socks, viz. cotton and viscose rayon, it was difficult to obtain complete solubility of the CECC yarns in these solutions. For example, when one of the socks was treated with a cold 1·5% aqueous solution of sodium hydroxide at a liquor ratio of 30 : 1, the CECC yarns were removed in about 10 min. In this instance, however, these yarns did not completely dissolve, but parted from the sock in the form of small highly swollen irregular lumps. The addition to the aqueous sodium hydroxide of soap and other paraffin-chain salts (0·1% based on the weight of solution) failed to bring about complete solution of the CECC yarns. Indeed, the time taken to bring about removal of the CECC yarns from the socks was increased appreciably when these additions were made.

It was considered that the lubricating oil used to facilitate the knitting operation might be restricting solution. With this possibility in mind,

the socks were given a scouring treatment prior to immersion in the aqueous sodium hydroxide solution Several mild scouring treatments were examined in which soap or a secondary alkyl sulphate such as Teepol was found to be satisfactory.

In each case two socks were treated with a 0·1–0·2% aqueous solution of the paraffin-chain salt for 5 min. at 40°C. and a liquor ratio of 50 : 1. On removal from the scouring solutions, the socks were well rinsed with distilled water. One sock was then dried at 80°C. for 2 hr. and the other was centrifuged to retain its own weight of water.

The dry sock was then immersed in a 1·25%, and the wet sock in a 1·3%, sodium hydroxide solution, in each case at a liquor ratio of 30 : 1 and a temperature of 20°C. It was noted that the CECC drawthread was completely dissolved, and the sock was then removed, rinsed, and dried. The results of two such trials are given in Table II.

TABLE II

Effect of Prescouring Treatment on the Solubility of CECC Yarns

Scouring Treatment	Time (min.) to remove the CECC Yarn	
	Dry Sock	Wet Sock
Unscoured	Not complete in 30	Not complete in 30
0·1% Soap... ...	12 (complete solution)	10 (complete solution)
0·2% Teepol (Shell)	11 (complete solution)	10 (complete solution)

It will be noted that scouring off the knitting oil permits complete dissolution of the CECC yarn.

Physical examination of the viscose rayon and cotton yarns after the various treatments showed no significant alteration in yarn strength and extensibility; shrinkage likewise was insignificant.

The resistance to stretching of nylon welts was a characteristic of the first nylon stockings. It was found that the plaiting of a scaffolding thread[11] with the nylon yarn produced a welt possessing improved elasticity. As nylon has an extremely high resistance to chemical attack, it was not considered that a cold 1·25% aqueous sodium hydroxide solution, necessary to dissolve CECC yarn, would have any ill-effect on nylon yarn. Nevertheless, in order to establish this point some 100-denier/36-filament CECC yarn was doubled with 70-denier nylon, thrown 4 turns "Z" twist, and knitted into stockinet. To remove the CECC yarns completely from the stockinet, the latter was soaked in a 1·25% aqueous sodium hydroxide solution at 20°C. for 10 min.; the CECC yarns appeared to be completely dissolved in 5 min. After 10 min. the stockinet was removed from the solution, rinsed thoroughly with water to remove completely the caustic alkali, and finally soaped for 5 min. in a 0·1% Lux solution at 40°C., rinsed in water, and dried.

TABLE III

Effect of Removal of CECC Yarn on Nylon

Nylon Yarn	Breaking Load (g.)	Extension (%)
From bobbin	298	13·3
From stockinet after treatment in 1·25% NaOH	302	17·7*

* The greater extensibility of the nylon yarn in the stockinet is due to contraction in the scouring process.

Comparative strength tests on the 70-denier nylon as received and the nylon in the stockinet after removal of the CECC yarn were then made (Table III).

From these tests it is clear that cold 1·25% aqueous sodium hydroxide solutions, necessary to cause dissolution of CECC yarns, have no effect on the strength of nylon yarn.

Note on the Dyeing Properties of CECC Yarn

The dyeing properties of yarns which have to be removed subsequently from fabrics do not seem to be of much importance; consequently the behaviour of CECC yarns towards dyes has not been fully investigated. Nevertheless, a preliminary examination of the dyeing behaviour of direct cotton dyes has been carried out, and a comparison made with the behaviour of these dyes on viscose rayon and calcium alginate rayon yarns.

As might be expected from their high water imbibitions, the rate of absorption of direct dyes by CECC and calcium alginate yarns is considerably higher than by viscose rayon yarn of the same denier. The dye absorption of CECC yarns is of the same order as calcium alginate yarn, and is so rapid that, even in the absence of common salt, dyebaths are very quickly exhausted.

The migration of direct dyes on CECC yarns is widely different from that of the same dyes on viscose rayon yarn. Many dyes which possess excellent levelling properties on cotton and viscose rayon, i.e. Class A dyes (cf. S.D.C. classification[12]), have very poor levelling properties when dyed on CECC yarns. On the other hand, there are a few instances where the opposite is true. Thus, certain Class C dyes, which normally possess poor migration properties on cotton and viscose rayon, show good levelling properties on CECC yarns. An example of a dye which exhibits this property is Direct Fast Orange WS (CAC).

In general, therefore, the high rate of dye absorption and the poor levelling properties of the majority of direct dyes on CECC yarns necessitate very careful selection of dyes, as otherwise uneven results are obtained. This would be especially so in the case of large-scale dyeing operations. The behaviour of direct dyes on CECC yarns differs markedly from that on cotton and viscose. Consequently, a special classification would be necessary for the successful application of these dyes to this fibre.

The dyeing of CECC yarns in boiling dyebaths is accompanied by a length shrinkage of about 35% and a considerable lateral swelling of the yarn.

Concerning the fastness to light of direct dyes on CECC yarns, we have found that this is of the same order as that of the same dyes on viscose rayon yarns. The wash-fastness, on the other hand, was found to be inferior to that of the same dyes on viscose rayon yarns.

The authors are indebted to the directors of Messrs. Courtaulds Ltd. for permission to publish

the results of this investigation. They also desire to thank their colleagues, Messrs. L. Rose and W. R. Weigham of Courtaulds Ltd., Coventry, for much help and advice in all matters concerned with the spinning of the cyanoethyl cellulose yarns.

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(Received 23rd June 1950)

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[12] *First and Second Reports of the Committee appointed by Council to discuss the Dyeing Properties of Direct Cotton Dyes* (reprinted from J.S.D.C., **62**, 280–285 (1946) and **64**, 145–146 (1948)).

CORRESPONDENCE

The Editor does not hold himself responsible for opinions expressed by correspondents

The First British Dyer of Turkey Red

The Editor

SIR,

Further to my letter of 29th September 1950[1], I have since found that, whereas Papillon in 1790 obtained a premium from the Commissioners and Trustees for Manufactures in Scotland for communicating the details of his process of dyeing Turkey Red to Dr. Black on condition that it should not be divulged for a certain term of years[2], Borell had made known his process four years earlier[3].

The wrongful impression that Papillon was the first man to dye Turkey Red in Britain comes from a mistaken reading of Ure's notes to his translation of the Berthollets' book, where he states[4]—"The first person who established, in this country, a factory for dyeing the Adrianople madder-red, was M. Papillon". Ure was a professor at Glasgow, and there is no doubt that by "this country" he meant Scotland and not Great Britain.

Yours truly
C. O. CLARK

THE PRIORY
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YORKS.

1st December 1950

[1] J.S.D.C., **66**, 546 (Oct. 1950).
[2] Berthollet, C. L. and A. B., *Elements of the Art of Dyeing*, translated by Ure, **2**, 378–379 (London 1824).
[3] "Report on Louis Borell's Petition for a Reward for discovering his Method of Dyeing the Colour of Turkey Red upon Cotton Hanks and in the Piece", *House of Commons J.*, **41**, 467 (3rd April 1786).
[4] Berthollet and Ure, *op. cit.*, **2**, 145.

Notes

Proceedings of the Council

At a meeting of the Council, held at the offices of the Society, 32–34 Piccadilly, Bradford, on 13th December 1950, the proceedings included the following items of interest—

MEMBERSHIP OF JUNIOR BRANCHES— It was noted that the Society's Bye-laws prescribed no age limit for membership of Junior Branches, but it was recommended that the age limit for participation in competitions organized by Junior Branches should be 25 years.

BRADFORD JUNIOR BRANCH— It was reported that Mr. K. Ascough had resigned as Honorary Secretary of the Bradford Junior Branch and that his position had been taken by Mr. J. Friend. Mr. C. S. O'Brien remained Chairman, while Miss M. Forbes had been elected Vice-chairman.

INTERNATIONAL FASTNESS WORK— It was reported that a progress report on this work (see J.S.D.C., **66**, 261 (May 1950)) would be submitted to the meeting of the I.S.O. Technical Committee on Textiles to be held in Bournemouth on 4–9th June 1951.

TERMS AND DEFINITIONS COMMITTEE— It was reported that Mr. S. R. Cockett and Mr. H. A. Turner had accepted the invitation to serve on this committee.

YORKSHIRE COUNCIL FOR FURTHER EDUCATION: COUNTY ADVISORY COMMITTEE FOR TEXTILES— Mr. A. Thomson was nominated to represent the Society on this Committee.

NOMINATION OF PRESIDENT— Mr. F. Scholefield was unanimously nominated for re-election as President for a second year (1951–52).

COMPOSITION OF THE COUNCIL— It was reported that four Vice-presidents (Mr. N. Hamer, Dr. H. H. Hodgson, Professor J. B. Speakman, and Mr. F. M. Stevenson) and four Ordinary Members of Council (Messrs. G. B. Angus, J. Boulton, C. O. Clark, and W. Penn) were due to retire in 1951. It was decided that one unfilled casual vacancy for a Vice-president should be filled by election for one year only.

NOMINATION OF OFFICERS— Mr. H. Jennison and Mr. J. Barritt were nominated for re-election

as Honorary Secretary and Honorary Treasurer respectively.

MEMBERSHIP — Twenty-four applications for ordinary membership and four for junior membership were approved.

Meetings of Council and Committees
January

Council— 10th
Finance— 10th
Publications— 16th
Colour Index Editorial Panel— 9th
Fastness Tests Co-ordinating— 17th
Diploma— 23rd
Review of Textile Progress— 19th

Deaths of Members

We regret to report the loss by death of Mr. L. Thompson and Mr. T. Saville Whittle.

Eighth Mercer Lecture

The eighth Mercer lecture will be given by Dr. D. Traill on *Protein Fibres with special reference to Man-made Fibres* at the St. Enoch Hotel, Glasgow, in Friday, 20th April 1951.

Second George Douglas Lecture

Arrangements have been made for the second George Douglas lecture to be given by Dr. G. P. Hoff, Manager of the Acetate Division of Messrs. E. I. du Pont de Nemours & Co. Inc., at the Midland Hotel, Manchester, on Tuesday, 8th May 1951.

A Study of Drying

The Institute of Fuel (18 Devonshire Street, London W.1) is organizing a comprehensive series of papers followed by discussions to cover all aspects of drying. The group of papers listed below will be of particular interest to readers of this *Journal*, and will be given in Manchester (at the Engineers' Club) on Tuesday, 6th March, and in Bradford on Wednesday, 14th March 1951, at 10.30 a.m. and 2 p.m.

Drying in the Textile, Paper, and Allied Industries	... R. R. Clegg
Drying in the Paper Industry ...	A. W. Western
Baking Crease-resisting Finishes	J. Sharpe
Drying of Dyed Viscose Rayon Cake	H. W. Best-Gordon
Migration of Dyes during Dyeing ...	... R. W. Speke
Accelerated Cylinder Drying ...	... E. H. Jones
Aspects of Circulatory Drying ...	F. W. Thomas
Stentering Machines	S. F. Barclay
Drying in the Photographic Industry	... A. K. Soper
Wool Drying	To be announced

The final conference is to be held at the Institution of Electrical Engineers, London, on Wednesday, 25th April 1951, at 10.30 a.m. and 2.30 p.m., when it is hoped to summarize the papers and discussions of the various sections.

Manufacturers' Publications and Pattern Cards

The Society does not accept any responsibility with regard to the statements in the following notes. Any publication abstracted may be referred to by members of the Society on application to Dr. C. B. Stevens, Dyeing Department, Leeds University

Allied Colloids (Bradford) Ltd.
TEXTILE AUXILIARY PRODUCTS

The following circulars have been issued by the Badische Anilin- und Soda-Fabrik (B.A.S.F.), Ludwigshafen, each dealing with either the properties and general application of an individual product or its use for a particular purpose. The first list comprises products belonging to ranges which were sold in Great Britain by the I.G. in 1939—

APPRETAN AX 45, C NEW, K PDR., LN 25, and WL CONC. NEW— Finishing agents.
BLANKIT (sodium hydrosulphite)— Separate circulars for its use in the textile trade and for bleaching edible oils and fats, glue, molasses for pressed yeast, soap, starch, raw sugar, and refined sugar.
BLANKIT I — Bleaching, reducing, and stripping agent.
BURMOL— Separate circulars for general textile use and for stripping garments.
CYCLANON LP CONC. POWDER AND WW DOUBLE CONC. (cf. J.S.D.C., **55**, 506 (1939))— Detergents.
DECROLIN SOLUBLE CONC.— Separate circulars for bleaching glycerol and soap.
DIAZOPON A— For improving fastness to rubbing of azoic dyeings.
DULLIT SL— Delustrant.
EMULPHOR A OIL-SOLUBLE, EL, FMR OIL-SOLUBLE, AND O— Emulsifying agents.
EULYSIN A— Crabbing and scouring assistant and dye solvent.
KAUBIT 140 AND KF PASTE— Anti-crease finishing agents.
LAVENTIN WR— Scouring assistant.
LEONIL LS, O SOLUTION, S, AND SBS PASTE HIGH CONC.— Wetting agents.
LUDIGOL— Dyeing and printing assistant.
NEKAL AEM, BX DRY, AND BX EXTRA STRONG (cf. J.S.D.C., **55**, 269 (1939))— Wetting agents.
PEREGAL O— Assistant in vat dyeing.
PERSISTOL NO— For water-repellent finishes.
RAMASIT I— Sizing and finishing agent; K CONC., KGT CONC., WD CONC., AND WDS DOUBLE CONC.— For water-repellent finishes.
RONGALIT C— Discharging agent.
SETAMOL WS— For reserving silk in wool dyebaths.
SOROMIN A BASE 100%, AF 100%, MW, SG 100%— Finishing agents for rayon.
TRILON A NEW POWDER AND B POWDER— Water-softening and metal-sequestering agents.
VEGAN SALT A— For preventing reduction of cotton dyes in one-bath union dyeing.

The following are post-war products—

BLANKOPHOR WT HIGH CONC.—Fluorescent bleaching agent.
LUFIXAN A— Fixing agent for direct cotton dyes.
NEKANIL A EXTRA— Wetting agent.
PRINTING OIL II— A mineral oil composition for use in printing pastes.
RAPID WETTING AGENT BASF— Wetting agent.
SPINNING OIL-ROTTOX— Spinning lubricant.
TEXTILE WAX WL— A water-soluble wax.
TONALON G AND T— Water-soluble alumina products for showerproofing textiles and improving the fastness to rubbing of azoic dyeings.

Imperial Chemical Industries Ltd.
Dyestuffs Division

WATER SOLUBLE THIONOL DYESTUFFS— This pattern book illustrates a range of ten solubilized sulphur dyes, including, in addition to the usual browns and blacks, a blue, a navy blue, and a green, all distinguished by the brand letter "M". Compared with the normal Thionol dyes, the M brands dissolve in water to give relatively stable solutions, although sodium sulphide and soda ash must be added before dyeing, as the dyes themselves have no affinity for cotton in aqueous solution. Advantages claimed include better level-dyeing properties, less tendency to give bronzy dyeings, particularly with blues, and less

sodium sulphide required for their application. The solubility in water of these dyes renders them particularly suitable for dyeing in circulating-liquor machines and makes possible the use of a pad–reduction method of application for materials otherwise difficult to penetrate and dye evenly. Certain dyeings can be aftertreated by the normal copper–chrome method to improve their fastness to light and wet treatments.

BRENTOGEN DEVELOPER N—This product (β-diethylaminoethanol) is a liquid which will dissolve Brentogen dyes without the use of caustic soda and has been introduced to enable full development of this class of dyes to be obtained in printing under neutral steaming conditions, whereas hitherto it has been necessary to employ acid steaming in the presence of caustic soda. The introduction of Brentogen Developer N also enables the printer to apply simultaneously vat dyes, while Soledon dyes, usually applied by the chromate acid steam method, can now be developed alongside the Brentogens under neutral steaming conditions. Brentogen Rapid dyes applied by the conventional caustic soda recipe give dull colours under neutral conditions, but the use of Brentogen Developer N enables bright colours comparable to those obtained with acid steaming to be obtained.

CHLORAZOL BRILLIANT ORANGE 3RS—This direct dye yields very bright reddish oranges and is recommended for use alone and in mixtures on all forms of cellulosic material where brilliance of hue but not high fastness to light or wet treatments is required. Dyeings become a little yellower when crease-resisted, while their fastness to light is slightly improved. Some fastness grades on cotton include— Light 3, washing (mild five times at 40°C.) 2, water 2.

CHLORAZOL COPPER BLUE FBS—This direct dye yields bright reddish blues on all types of cellulosic materials when aftertreated on the fibre with copper sulphate. Dyeings on viscose rayon are redder than on cotton, and become redder still when crease-resisted. It may be applied in circulating-liquor machines and is of special interest for dyeing yarn for conversion into the cheaper types of woven fabric. It is of only limited interest for direct printing, but may be used for coloured grounds for white or coloured discharge styles. Some fastness grades on cotton (aftertreated with copper sulphate) include— Light 6, washing (mild five times at 40°C.) 3, water 4.

CHROMAZOL BRILLIANT BLUE 4GS—This is an acid mordant dye, particularly suitable for direct print and coloured Formosul discharge styles on cotton and viscose rayon to give bright blues of good wet fastness. It is also of some interest for printing alongside azoic combinations and on silk, where development of a harsh handle is prevented by including urea in the printing paste. Some fastness grades when directly printed on cotton include— Light 2–3, washing (mild five times at 40°C.) 3, water 3.

ULTRALAN BORDEAUX B—This premetallized dye is recommended for use from a strongly acid bath on all types of piece material, carpet yarns, and wool and fur felt to give dyeings of good fastness to wet treatments, including chlorination and carbonizing. Although of little interest for direct printing on wool, it may be discharged white using Formosul or Reduzol Z, and is thus of interest for producing dischargeable grounds. Some fastness grades on wool include— Light 6–7, chlorination 5, carbonizing 5.

ULTRALAN RED B—This further addition to the range of premetallized dyes is similar in dyeing behaviour and characteristics to Ultralan Bordeaux B (above). Unlike the latter, however, it is of interest for direct printing on wool in addition to being very suitable for producing dischargeable ground shades. Some fastness grades on wool include— Light 6, carbonizing 5, washing (mild five times at 40°C.) 3–4.

Reports on German Industry

I.G. Farbenindustrie A.-G., Hoechst a. M. Inorganic Chemicals, Fireproofing Agents "Luminous Blue" (Strontium Calcium Sulphide)

FD 1095/50* (PB 70,223; Microfilm O 16).

Replies to a questionnaire (15 questions for each product) on the composition, manufacturing details, etc. of a large number of inorganic products, among which are *Locron A* (42% $NH_4SO_3NH_4$, 52% $NH(SO_3NH_4)_2$, 3% NH_3, 3% $(NH_4)_2SO_4$), *R* (90% *S* + 10% NH_4HCO_3), and *S* (a mixture of ammonium amidosulphonate and imidosulphonate), used as fireproofing agents for textiles; and "Luminous Blue" (mixed crystals of strontium and calcium sulphides), used for marking and illuminating traffic ways. C. O. C.

I.G. Farbenindustrie A.-G., Frankfurt a. M. Recent Research on the Chemistry of Organic Fluorine Compounds up to the End of 1944

Scherer. FD 1076/50* (PB 52,185).

Microfilm of an English translation of an 11 pp. paper, which should be read in conjunction with FIAT 838, *Elemental Fluorine*. The various methods of preparing fluorine compounds and their uses, including use in making dyes, are reviewed. C. O. C.

I.G. Farbenindustrie A.-G., Hoechst a. M. Mowiliths, Appretans, Solvents, Plasticizers, Inorganic and Organic Chemicals, Deglykal A, Vinarol BO

FD 1094/50* (PB 70,223 and 70,172; Microfilms O 16 and O 17 respectively).

Replies to a questionnaire asking for information about chemical and trade names, chemical composition, manufacture, uses, etc. of a wide range of products, including numerous Mowiliths, several Appretans, solvents and plasticizers, inorganic and organic chemicals used as dyeing assistants or as intermediates for dyes or auxiliary agents; *Deglykal A* (glycollic acid partly neutralized with ammonia and mixed with 5% of Trilon A), a deliming agent used in the leather industry; and *Vinarol BO* (50% Vinarol 50 B, 25% Vinarol 50, and 25% Vinarol 30), used as a size for rayon. C. O. C.

I.G. Farbenindustrie A.-G., Ludwigshafen Aromatic Bases, Phenols, Halogenated Hydrocarbons, Aromatic Esters, Synthetic Resins, Aliphatic Nitriles, Hydrocarbons, Sulphonic Acids, Sulphones, Plasticizers, Nitro Compounds, etc.

FD 1116/50* (PB 70,058).

Microfilm copy of numerous reports (531 pp.), in German and dated 1934–36, on the manufacture and uses of a large number of organic chemicals. C. O. C.

Reichsamt für Wirtschaftsausbau, Berlin Developments in the Production of Cellulosic Rayon

FD 1070/50* (PB 52,006).

Microfilm (123 pp.) of papers, and discussions on them, read at a meeting of the Working Committee for Textile Fibres in 1940. They are—

(1) *Developments in Production of Cellulose* (Schepp)
(2) *New Sources of Cellulose* (W. Scheiber)
(3) *Influence of Methods of Preparation on the Properties of Cellulose and Staple Fibre* (Dörr)
(4) *Current Problems in Producing and Improving Staple Fibre* (J. Kleine)
(5) *Saving of Chemicals in the Spinning of Viscose Rayon* (Bauer)
(6) *Problems and Present Position of Cuprammonium Rayon Production* (Elsässer)
(7) *Problems and Present Position of Acetate Staple Fibre Production* (Gruber)
(8) *Comparative Studies on Various Types of Cellulose* (Eisenhut)

* Material available for inspection at, and photocopies available from, T.I.D.U., Board of Trade, Lacon House, Theobalds Road, London W.C.1 or (under PB No.) from Office of Technical Services, Department of Commerce, Washington D.C., U.S.A.

(9) *Problems connected with the Improvement of Staple Fibre* (H. Rath)
(10) *Significance and Present Position of Research on Wool Fibres* (J. Nüsslein). C. O. C.

Arbeitsstab Chemische Forschung und Entwicklung, Berlin
Asbestos, Glass Fibres, Polyvinyl Compounds
FD 1106/50* (PB 52,025).

Microfilm copy of the *Reichsberichte für Chemie* (1, No. 2 (1st July 1944)). It contains lectures on natural and synthetic asbestos and its uses, and on the production of glass fibres. These are followed by several patent applications which had been hitherto kept on the secret list; they include the two following—

Esterified Hydroaromatic Carboxylic Acids as Solvents, Swelling Agents, Gelatinizing Agents, and Plasticizers for Vinyl Polymers, Deutsche Hydrierwerke A.-G., *G.P. Application* D 90,175, IVc/39b (5th March 1943).

Modifying Polyvinyl Alcohols and their Derivatives by use of Dianil or Diamine Dyes, Dr. A. Wacker G.m.b.H., *G.P. Application* W 113,406, IVc/39b (21st June 1943). C. O. C.

I.G. Farbenindustrie A.-G., Hoechst a. M.
Analytical Methods for Plastics and Textiles
FD 1099/50* (PB 70,188; Microfilm O 37).

A collection of 17 methods, including the following determinations—

(1) Aluminium and chlorine in the fibre
(2) Grease in wool
(3) Casein fibres in mixtures
(4) Urea–formaldehyde resins on the fibre
(5) Hydroxymethylureas in connection with the use of a formaldehyde–urea–alum solution as a delustring agent.

The other methods deal with the analysis of plastics. C. O. C.

* Material available for inspection at, and photocopies available from, T.I.D.U., Board of Trade, Lacon House, Theobalds Road, London W.C.1, or (under PB No.) from Office of Technical Services, Department of Commerce, Washington D.C., U.S.A.

Abstracts from British and Foreign Journals and Patents

(*The Titles of Patents are abridged and modified*)

I—PLANT; MACHINERY; BUILDINGS

PATENTS

Apparatus for Producing Channel Carbon Black. R. B. Takewell and J. M. Huber Corpn. *U.S.P.* 2,518,094.

Pelleting Furnace Blacks. W. B. Wiegand, C. W. Sweitzer, and Columbian Carbon Co. *U.S.P.* 2,518,211.

Continuous Wet Treatment of Tows. J. E. Spalding, L. K. Spangler, and American Viscose Corpn. *U.S.P.* 2,516,268.

Continuous Liquid Treatment of Threads. Courtaulds Ltd., J. H. Givens, J. Wale, and L. Rose. *B.P.* 645,171.

The roller on which aqueous liquid treatment of the threads is to be carried out has its surface divided into at least one liquid-treating zone and a boundary zone whose surface is not wetted by the liquid used, so that the liquid fed to the treating zone will not normally pass across the boundary zone. Suitable materials for such boundary-zone surfaces are polythene and polytetrafluoroethylene. C. O. C.

Preparation and Distribution of Sizing Materials. G. J. Kyame and U.S. Secretary of Agriculture. *U.S.P.* 2,516,884.

Coating or Impregnating Yarns with Plastics. Fassoply Ltd. and D. J. Lodge. *B.P.* 645,727.

The coated or impregnated yarn is drawn through a bath of mercury, which acts as an infinitely variable die or squeeze and removes surplus coating or impregnating liquor from the yarn. The coating or impregnating bath may float on top of the mercury. C. O. C.

Treating Fabrics with Liquids. Sellers & Co. (Huddersfield) Ltd. and E. R. Sellers. *B.P.* 646,616.

Modification of *B.P.* 629,310 (*J.S.D.C.*, **66**, 151 (Feb. 1950)). Fabric being treated in rope form is passed between nip rollers hydraulically weighted so that the upper roller exerts any desired pressure on the lower roller. It then passes down a trough or spout having a weighted, pivoted lid, the weighting of the lid being effected by the hydraulic system of the machine. The principle is very suitable for application to milling or scouring machines. C. O. C.

List-opening Apparatus. C. H. Turner. *B.P.* 644,987.

A list-opening device is described which removes creases, folds, or rolls from the selvedges, so that they can be fed flat on to a tenter or other machine. C. O. C.

Cloth Guides. Mount Hope Machinery Co. *B.P.* 646,566.

The selvedges are engaged by pairs of rolls which tilt when the selvedge moves from its set path. This tilting of the rolls is responsive to frictional engagement of the selvedge with a rotary element, which in one form remains fixed in its position of rotation regardless of any tilting of the rolls, and in another form moves with the rolls as they tilt. Such guides are very sensitive and impart little appreciable increase in the drag imposed on the cloth by the rolls. C. O. C.

Overfeed and Internal Expander for Tubular Fabric. F. C. Wedler and American Viscose Corpn. *U.S.P.* 2,517,067.

Apparatus is described which uniformly spreads and stretches tubular fabric. C. O. C.

Affixing Fabrics to Printing Blankets. W. Geiringer. *B.P.* 646,172.

The fabric is gummed on its back before it is passed to the endless blanket at the end of the printing table, suitable apparatus being described. C. O. C.

Box Wheels for Printing Machines. Bollington Printing Co. Ltd. and A. Lewis. *B.P.* 645,782.

Nylon Hose Preboarding Machine. Paramount Textile Machinery Co. and H. Richter. *B.P.* 644,461.

A vertical retort has an upright reversible door which rotates about a vertical axis. A series of metal hosiery shapes are mounted on both faces of the door, enabling one series of forms to be loaded whilst the opposite series are in the chamber. There is an automatic electrical timing control of the steaming period, exhaustion of the chamber being initiated when the door closes, and means are provided for passing a stream of cool air into the loading area. G. E. K.

Presetting Cabinet for Nylon Hose. Paramount Textile Machinery Co. and H. Richter. *B.P.* 645,427.

A hosiery-carrying truck with hose suspended from hanger racks is introduced into a cabinet. Manual closing of the door initiates a sequence of automatically controlled operations, viz. introduction of steam with operation for a fixed period after a predetermined temperature has been reached followed by exhaustion of the steam accompanied by admission of air under pressure to the chamber. A warning system signals the conclusion of the operations. G. E. K.

Hardening Felt Hat Bodies. Merrimac Hat Corpn. *B.P.* 646,064.

A fully automatic machine is described which gives better and more uniform hardening than has been hitherto obtainable. C. O. C.

Spotting Board. F. H. Richterkessing. *B.P.* 644,937.

The spotting board comprises a rigid hairpin-shaped frame mounted over a like-shaped trough, into which hot air or steam may be introduced as required. The frame encloses a perforated metal screen covered by a fine wire

mesh. Stainless steel is preferred in the construction of the machine. G. E. K.

Apparatus for Impregnating Garments, etc. A. C. Smith and Pennsylvania Salt Manufacturing Co. *U.S.P.* 2,516,349.

Opening Skins. Belden Manufacturing Corpn. and J. A. Hassan. *B.P.* 645,840.

A skin-opener comprises a frame on which an elongated pointed bar is mounted. The closed skin is slid along this bar from its pointed end. The bar has a longitudinal slot in its surface inwardly from the pointed end. A rotary vertical knife disc is mounted over the bar in alignment with the slot. The knife disc is adjustable to and from the bar, which itself is longitudinally adjustable along its mounting. C. O. C.

Coating Articles by Electrostatic Deposition. H. J. Ransburg, H. G. Ransburg, H. P. Ransburg, E. M. Ransburg, Harper J. Ransburg Co., and R. E. Helmuth. *B.P.* 645,612.

II—WATER AND EFFLUENTS

Algæ and Deposition of Calcium Carbonate. H. Ingleson. *Surveyor*, **108**, 698 (1949): *Water Pollution Abs.*, **23**, 31 (Feb. 1950).

Formation of $CaCO_3$ scale reduced the rate of delivery of a pump taking water from an impounding reservoir. Analysis of water from the two streams feeding the reservoir and from the pump sump showed that water leaving the reservoir was considerably more alkaline than that entering it. Apparently algæ in the reservoir removed CO_2 during photosynthesis, thus rendering the solution of $CaCO_3$ unstable. Where it is impossible to add an algicide to such a reservoir, addition of sodium hexametaphosphate to the water in the pump sump should prevent precipitation of $CaCO_3$. C. O. C.

Boiler-water Treatment. H. Reichelt. *Chemie Ing. Tech.*, **22**, 290–292 (1950): *Chem. Abs.*, **44**, 9093 (10th Oct. 1950).

A combination of treatment with an NH_4–anion exchanger and lime softening of residual bicarbonate hardness is described and results are given. C. O. C.

Wool Scouring and Dyeing Wastes Treatment Plant. S. E. Coburn. *Water & Sewage Wks.*, **97**, 167–171 (1950): *Water Pollution Abs.*, **23**, 45 (Feb. 1950).

The waste scouring and dye liquors of a carpet mill at Glasgow, Va., are passed to separate equalization tanks, and then discharged together into a tank, where H_2SO_4 is added to adjust the pH and coagulate grease and colloidal matter. After passing through flocculating and sedimentation tanks, the waste waters are treated with hydrated lime, which may be lime sludge from the softening plant, before discharge into a river. Ferric sulphate may be added to the acid wastes or to the waste water after neutralization if an additional coagulant is necessary. Sludge is pumped to sludge lagoons, and supernatant liquor from the sludge to the equalization tank receiving spent dye liquor. On the average, the B.O.D. (biological oxygen demand) of the mixed effluents was reduced from 2260 to 915 p.p.m., and suspended solids were reduced from 3793 to 156 p.p.m. C. O. C.

Effect of Hexametaphosphate on Pitch Troubles in Paper Mills. G. Gavelin. *Pulp Pap. (Mag.) Can.*, **50**, (10), 109–115 (1949): *Water Pollution Abs.*, **23**, 31 (Feb. 1950).

Hexametaphosphate added to the white water to reduce deposition of pitch is more effective with mixtures of sulphite and groundwood pulps as the sulphite pulp content decreases. Apparently effectiveness is not due to reaction of hexametaphosphate with the dispersed pitch but to formation of a film which prevents adhesion of the pitch to the walls of the white water system. At a concentration of 10 mg. of Calgon per litre and at pH 5 the wet strength of paper was increased owing to a sizing effect. Tables and graphs giving the results of investigations into the factors affecting this sizing effect are given. C. O. C.

Critical Review of the Literature of 1949 on Sewage and Waste Treatment and Water Pollution. W. Rudolfs *et al.* *Sewage & Ind. Wastes*, **22**, 593–653 (1950).

398 References are given. C. O. C.

PATENT

Decolorizing Water of High Colour due to Organic Matter. R. Burns, S. M. Farrer, and I.C.I. Ltd. *B.P.* 645,295.

Some waters, particularly surface waters of moorland type, even after coagulation and filtration are not entirely free from colour, which often intensifies on heating. By treating the water with hydrogen peroxide with or without chlorine before adding the coagulants the residual colour is much reduced and does not appreciably increase on boiling. C. O. C.

III—CHEMICALS; AUXILIARY PRODUCTS; FINISHING MATERIALS

PATENTS

Esters of Polyoxyalkylene Monoethers—Lubricants. Carbide & Carbon Chemicals Corpn., H. R. Fife, and F. H. Roberts. *B.P.* 644,828.

The alkyl monoethers of copolymers of ethylene oxide (1 part by wt.) and propylene oxide (0·3–9·0) of mol. wt. > 500 are esterified by heating with a carboxylic acid of 2–20 C, e.g. acetic, stearic, or benzoic acid, or its anhydride or chloride. The products have high viscosity indices and are suitable as plasticizers and textile lubricants. E. C.

Dry Stabilized Hydrosulphite. L. C. Hurd, G. C. Riley, and Röhm & Haas Co. *U.S.P.* 2,516,321.

A mixture of sodium tetraborate (3–10 parts), paraformaldehyde (3–10 parts), and sodium hydrosulphite (94–80 parts) remains active and non-caking or lumping even on prolonged storage. In use it is sufficiently stable at the boil to allow efficient stripping. C. O. C.

Stabilization of Hydrogen Peroxide. du Pont. *B.P.* 645,225.

The stability of a hydrogen peroxide solution, particularly one of > 50% by weight, is at a maximum at or close to its "neutrality pH" and rapidly decreases as the pH is raised or lowered therefrom. The effect of stabilizers is also greatest at or near the "neutrality pH", which is determined by titrating two samples of H_2O_2 with acid and alkali respectively and plotting the pH against the additions of acid or alkali. The point at which the greatest change in pH takes place for an infinitesimal unit amount of alkali or acid added gives the "neutrality pH". C. O. C.

Stilbene Derivatives for Use in Whitening Textiles. R. H. Wilson and I.C.I. Ltd. *B.P.* 645,413.

The 4:4′-bistriazinylaminostilbene-2:2′-disulphonic acid compounds containing dimethylamino or morpholino groups attached to the triazine nuclei have a whitening effect on textiles superior to that obtained with the previously known derivatives of 4:4′-diaminostilbene-2:2′-disulphonic acid. They are produced by treating 2 mol. of cyanuric chloride with, in any order, 1 mol. of 4:4′-diaminostilbene-2:2′-disulphonic acid or a salt thereof, 2 mol. of dimethylamine or morpholine, and 2 mol. of a primary or secondary aliphatic amine containing no hydroxyl group or of a primary aromatic amine which is either unsubstituted or contains as nuclear substituents one or more Alk and/or an $O{\cdot}CH_3$ or an $SO_3{\cdot}NH_2$ radical. C. O. C.

Shrink-resisting and/or Water-repellent and/or Softening Agents. W. Baird, T. Barr, E. S. Lane, A. Lowe, and I.C.I. Ltd. *B.P.* 645,138.

Compounds of formula—

$$(HO{\cdot}CH_2{\cdot}NH{\cdot}CO{\cdot}O)_m R(O{\cdot}CO{\cdot}NH{\cdot}CH_2{\cdot}A\}X)_n$$

(R = subst. or unsubst. hydrocarbon; A = aliphatic or heterocyclic tertiary amine; X = univalent anion; $m = 0$ or a whole number; n = a whole number; $m + n > 1$) when impregnated into animal or vegetable textiles from aqueous dispersion or organic liquid solution, the textiles then being dried and subsequently heated to decompose the compound, e.g. to 150°c., impart water-resistance and/or water-repellency and/or softness. The preparation of such compounds is described. C. O. C.

Stable Aqueous Emulsions of Formaldehyde–Amide–Alcohol Condensates. Ciba Ltd. *B.P.* 645,023.

A water-insoluble heat-hardenable condensate, soluble in organic solvents, of (i) formaldehyde, (ii) a substance of

amide character, capable of forming a hardenable aminoplast with the formaldehyde, e.g. urea, and (iii) a water-immiscible alcohol is emulsified in water in the presence of a protein, e.g. casein, and urea and/or thiourea. Application of such emulsions to paper, leather, textiles, etc. followed by a short heat-treatment results in water-resistant effects.

B.P. 645,926.

An aqueous colloidal solution of at least one water-soluble colloidal substance which will inhibit migration, e.g. tragacanth, starch, carob-bean meal, or polyvinyl alcohol, is added to the emulsion. C. O. C.

Uniformly 2-Substituted Glucopyranose Polymers. K. M. Gaver and Ohio State University Research Foundation. *U.S.P.* 2,518,135.

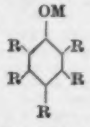
2-Monoalkyl ethers of starch, useful as adhesives, wetting agents, detergents, emulsifying agents, sizes, etc., are obtained by treating starch with an alkali-metal hydroxide at 78–98°C. in an anhydrous alcohol of b.p. > 78°C. The alcoholic mixture is then treated with a salt which dissociates at 78–115°C. in a non-aqueous system, e.g. ethereal salts, non-metal and metal salts except salts of alkali metals and ammonia, so that the salt cations replace the alkali-metal cations. C. O. C.

Water-dispersible Pastes of Gas Fume Fading Inhibitors for Acetate Rayon Dyes. F. H. Smith and du Pont. *U.S.P.* 2,518,393.

NN'-Diphenylethylenediamine and related gas fading inhibitors are obtained as stable pastes, which do not dry out excessively when exposed to air during normal use, by dispersing them in an aqueous mixture containing polyvinyl alcohol or methyl cellulose and an oil-like high-boiling non-volatile water-immiscible liquid. C. O. C.

Casein Coating, Sizing, and Finishing Compositions. D. F. Holloway, H. H. Young, and Swift & Co. *U.S.P.* 2,516,700.

A composition which is immune to bacterial decomposition and which can be infinitely diluted at pH 7 or lower without precipitation of water-insoluble protein consists of casein or water-insoluble vegetable protein (15–35 parts by wt.), urea (15–35), water (25–50), and a mono alkali-metal salt (1–5) of formula—



(R = H, OH, Hal, NO_2, Alk, Ar, alkaryl, alkoxy, or aroxy; M = alkali metal), e.g. sodium pentachlorophenoxide. C. O. C.

Water- and Flame-proofing Composition for Textiles and Paper. J. F. McCarthy and Treesdale Laboratories Inc. *U.S.P.* 2,518,241.

A composition consisting by weight of 42% of a mixture of chlorinated paraffins of 70 and 42% chlorine content respectively, 4·5–6·5% of a soluble, fusible, unmodified phenol–formaldehyde resin, 22–24% of finely divided $CaCO_3$, 14·7–19·7% of Sb_2O_3, 1% of aluminium stearate, and 7–14% of an aromatic hydrocarbon solvent renders textiles impregnated with it water- and flame-proof, mildew- and rot-resistant, and particularly resistant to laundering and weathering. C. O. C.

Bactericidal and Fungicidal Composition. Buckman Laboratories Inc., S. J. Buckman, and R. N. Meals. *B.P.* 645,409.

A mixture or compound of a trichlorophenol or a salt thereof with a compound of formula R·HgX (R = a non-ionic radical, X = an anion), e.g. hydroxyphenylmercuric acetate, has powerful antiseptic properties. C. O. C.

Rot- and Mildew-proofing agents. Nuodex Products Co. Inc. *B.P.* 646,207.

The products obtained by reaction of C_8–C_{18} aliphatic water-insoluble amines with acids only one of which may be soluble in water, e.g. a multiple neutral salt of salicylic and lactic acids with n-dodecylamine, are highly efficient rot- and mildew-proofing agents. On being applied, e.g. to cotton, they are fairly resistant to leaching despite their solubility in water. C. O. C.

Aqueous Dispersions of Ethyl Orthosilicate. Silicon (Organic) Developments Ltd., D. A. W. Hill, C. Shaw, and W. E. Langrish-Smith. *B.P.* 644,908.

Aqueous dispersions of ethyl orthosilicate, which remain fluid for several weeks and are suitable for treating textiles to increase surface roughness and for reducing tack in uncured rubber, are prepared by emulsifying the ester and water using a non-metallic soap, e.g. triethanolamine oleate, as emulsifier and a water-softening agent, e.g. sodium metaphosphate. E. C.

Bleaching of Linseed Oil with Benzoyl Peroxide and the Influence of Certain Antioxidants. P. Colomb. (VII, p. 93.)

Methylsiloxanes as Water-repellent Finishing Agents. Société des Usines Chimiques Rhône-Poulenc. (X, p. 95.)

IV—RAW MATERIALS; INTERMEDIATES; COLOURING MATTERS

Demonstrability of the Photochemical Formation of Diradicals by Magnetic Methods. M. Born and A. Schönberg. *Nature*, 166, 307 (19th Aug. 1950).

The production of a crystalline peroxide from 5:6:11:12-tetraphenylnaphthacene (rubrene) by irradiation with sunlight or artificial light in presence of oxygen is discussed. Previous theories that this cannot proceed via an activated diradical because the essential paramagnetism of the latter has not been detected are considered invalid. Calculations are advanced to show that the activated diradical is almost certainly present in such small quantities that its paramagnetism cannot be detected by the method employed. J. W. B.

Occurrence of Hypsochromic Shifts on Alkyl Substitution—Structure and Colour of Methylated Derivatives of Azulene. B. Pullman, M. Mayot, and G. Berthier. *J. Chem. Phys.*, 18, 257–260 (1950): *Chem. Abs.*, 44, 9251 (25th Oct. 1950).

While two methylated derivatives of azulene show the usual bathochromic shift with respect to azulene itself, the remaining three isomers show unusual displacement of the visible spectrum toward shorter wavelengths. Steric effects cannot account for this effect, which is thought to be due to hypsochromic shifts brought about by alkyl substitution and to the structure of azulene and its derivatives. Molecular-orbital method calculations show that Mulliken's $N \rightarrow V$ colour theory accounts satisfactorily for the observed facts. In methylated derivatives showing bathochromic shift, the calculated excitation energy of the $N \rightarrow V$ transition seems to be smaller than the corresponding energy in azulene itself, the reverse being true for the compounds showing hypsochromic shift. The general conditions necessary for the occurrence of the hypsochromic shift upon alkylation are given. C. O. C.

Absorption of Certain Heterocyclics of the Naphthalene Series—II. E. Baltazzi. *Compt. rend.*, 231, 156–158 (1950): *Chem. Abs.*, 44, 9251 (25th Oct. 1950).

Absorption curves are given of alcoholic solutions of β-naphthylamine, *N*-phenyl-β-naphthylamine, 1-α-naphthyl-3-phenyltriazene, 3-naphtho(1:2)triazole, 1-, 2-, and 3-methyl- and 2- and 3-phenyl-naphtho(1:2)triazole. Their possible structures are discussed. C. O. C.

Grape-seed Utilization [in Dye, Lake, and Resin Making]. A. M. Frolov-Bagreev. *Vinodelie i Vinogradarstvo S.S.S.R.*, 8, (8), 15–16 (1948): *Chem. Abs.*, 44, 9700 (25th Oct. 1950).

Grape seeds yield 15% by weight of a semi-drying oil containing 8–13% palmitic and stearic acids, 80% linolenic and erucic acids, and traces of melissic acid and two C_{14}–C_{16} hydroxy acids. It is useful in making dyes, lakes, and resins. C. O. C.

Absorption Spectrum and Photodecomposition of o-Hydroxybenzenediazonium Sulphate. J. de Jonge, R. J. H. Alink, and R. Dijkstra. *Rec. Trav. chim.*, **69**, 1448–1454 (Nov. 1950).

The long-wave absorption maximum of *o*-hydroxybenzenediazonium salts in water is at 3950 A. and in 50% sulphuric acid is at 3500 A.; this shift may be due to the occurrence of resonance structures of nearly equal energy. Whereas the photodecomposition of *o*-hydroxybenzenediazonium sulphate in water gives a quantitative yield of *cyclo*pentadienecarboxylic acid, decomposition in 50% sulphuric acid yields mainly catechol. It is suggested that the effect of sulphuric acid, both on the spectrum and on the photodecomposition, is to increase the energy of the quinonoid resonance structure of the *o*-hydroxybenzenediazonium ion. H. H. H.

Organolead Compounds containing an Azo Linkage. H. Gilman and C. G. Stuckwisch. *J. Amer. Chem. Soc.*, **72**, 4553–4555 (Oct. 1950).

The preparation of several azo-lead dyes by coupling a diazonium salt with an aminoaryl- or hydroxyaryl-lead compound is described. C. O. C.

Antitubercular Activity of Azo Dyes. I—Bisazo Dyes derived from Tetrazotized Bis-4-aminophenyl Sulphone and Various Coupling Components. P. P. T. Sah. *Rec. Trav. chim.*, **69**, 1407–1434 (Nov. 1950).

Of 30 bisazo dyes, the *in vitro* activity against *M.Tb.* showed that the most active ones were derived from *m*-phenylenediamine, *m*-aminobenzoic acid, salicylic acid, and 8-hydroxyquinoline. The relationship between chemical structure and biological activity is discussed. H. H. H.

Antitubercular Activity of Azo Dyes. II—Monoazo Dyes derived from Diazotized Sulpha Drugs and Bis-4-aminophenyl Sulphone and Bisazo Dyes from Tetrazotized Bis-4-aminophenyl Sulphone and Sulpha Drugs. P. P. T. Sah and J. F. Oneto. *Rec. Trav. chim.*, **69**, 1435–1447 (Nov. 1950).

Biological tests indicate that the monoazo dyes are in general more active than the corresponding bisazo dyes, and, in turn, the latter are more active than the bisazo dyes of Part I (above). H. H. H.

Quinoneimides. I—*p*-Quinonedisulphonimides. R. Adams and A. S. Nagarkatti. *J. Amer. Chem. Soc.*, **72**, 4601–4606 (Oct. 1950).

p-Phenylenedibenzenesulphonamide and the di-*p*-toluenesulphonyl and dimethanesulphonyl derivatives of *p*-phenylenediamine, and the dibenzenesulphonyl derivatives of 2-methyl-, 2-chloro-, 2:5-dimethyl-, and 2:5-dimethyl-3-chloro-*p*-phenylenediamine are readily oxidized to stable *p*-quinonediimides. They resemble quinone in being readily reduced by various agents, and readily add HCl to yield the 2-chloro-*p*-phenylenedibenzenesulphonamides. C. O. C.

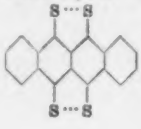
Photodynamic Action of Organic Dyes on Proteins. S. Fiala. *Chem. Listy*, **39**, 14–19 (1945): *Chem. Abs.*, **44**, 9493 (25th Oct. 1950).

Fluorescein, eosin, and erythrosin form labile combinations with oxygen. When illuminated, the dyes release activated O, which forms an O wave and oxidizes proteins of horse and human blood plasma at pH 8–8·62. The oxidizing agent is O. It cannot be H_2O_2, as the effect is not influenced by catalase. C. O. C.

The Structural Problem of the Tetracene Series [Pigments from "Acenes"]. C. Marschalk and C. Stumm. *Bull. Soc. chim. France*, 418–428 (1948): *Chem. Abs.*, **44**, 9399–9401 (25th Oct. 1950).

A detailed investigation of the properties and reactions of tetracene—

and its derivatives. Tetracene when refluxed with S in presence of trichlorobenzene yields a green pigment—



Facile formation of such sulphides is common to many linear polynuclear hydrocarbons ("acenes") and to many of their hydrogenation products. The pigment thus derived from naphthacene contains 4, that from pentacene or hexacene 6, S atoms per mol. After a critical analysis, and in some cases reinterpretation, the work of previous authors is exhaustively collated with the present work. C. O. C.

Arylamino Derivatives of Alizarin. R. P. Gonsalves, A. N. Kotharo, and V. V. Nadkarny. *J. Indian Chem. Soc.*, **27**, 479–483 (Sept. 1950).

Arylamino derivatives of alizarin have been prepared by condensing 4-nitroalizarin with (*a*) aniline, (*b*) *o*-nitroaniline, (*c*) *p*-nitroaniline, (*d*) *m*-nitroaniline, (*e*) *p*-toluidine, (*f*) *a*-naphthylamine, and (*g*) *β*-naphthylamine. Analysis shows that only one arylamino residue is introduced into the molecule in all cases. The presence of two free hydroxyl groups is substantiated by the alkali-solubility of these derivatives and by the formation of crystalline dibenzoyl derivatives in each case. By reducing the products formed with the nitroanilines, and benzoylating the amino compounds so produced, it has been shown that the introduction of arylamino and nitroarylamino residues into alizarin does not enhance its tinctorial strength. Work is proceeding on the dyeing properties of sulphonated arylaminoalizarins. A. S. F.

Progress in Pigment Dyes. J. Smethurst and W. Carr. *Paint*, **20**, 391–396, 408 (Nov. 1950).

A survey of recent developments in the manufacture of organic pigments together with a survey of the uses to which they are now being put, including their use in the textile and plastics industries. C. O. C.

Retinal Receptors. H. Hartridge. *Nature*, **166**, 820–821 (11th Nov. 1950).

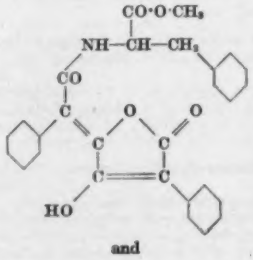
Retinal photopic pigments are discussed. It is suggested that they are chemically related, differing from one another by simple group substitution, which provides equal frequency intervals. The resulting response curves have crests very close to those of the retinal receptors. J. W. B.

New Pterins (Xanthopterin-B, Leucopterin-B, and a 6-Dehydroxyleucopterin Derivative) obtained from *Bombyx mori* (Silk Worm). Y. Hirata, K. Nakanishi, and H. Kikkawa. *Bull. Chem. Soc. Japan*, **23**, 76–80 (Aug. 1950).

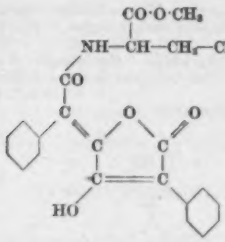
The epidermis pigments of *Bombyx mori* were investigated to elucidate the tryptophan metabolism. The following three new pterins were obtained from the respective races—(*a*) Normal type: leucopterin B, leucopterin. (*b*) Mutant "lem": leucopterin-B, xanthopterin-B, and leucopterin. (*c*) Mutant "od": leucopterin-B, leucopterin. (*d*) Unidentified white race: 6-dehydroxyleucopterin derivative. These compounds differed in their ultra-violet absorption spectra. The pterin nature of the epidermis pigments is thus established. H. H. H.

Structures and Syntheses of Rhizocarpic Acid and Epanorin. R. L. Frank, S. M. Cohen, and J. N. Coker. *J. Amer. Chem. Soc.*, **72**, 4454–4457 (Oct. 1950).

Rhizocarpic acid, the yellow pigment in *Rhizocarpon geographicum*, and epanorin, a similar pigment from *Epanora lecanora*, have the structures—



and



respectively. They are the only known nitrogen-containing lichen pigments. C. O. C.

Review of Pigment Progress [in 1949–50]. W. M. Morgans. *Paint*, **20**, 387–390, 400 (Nov. 1950).
A review with 61 references. C. O. C.

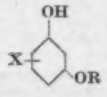
Dyed Aluminium Powder. G. W. Wendon. *Paint*, **20**, 397–400 (Nov. 1950).
An account of the production and properties of dyed aluminium powder. The fact that dyed flake aluminium, whether polished or not, is non-leafing is discussed with reference to its bearing on the theory of leafing. C. O. C.

Studies of Carbon Blacks. I—Properties of Various Types of Carbon Black. T. Sengoku, Y. Imanishi, T. Ikisu, and S. Nishizawa. *J. Soc. Rubber Ind. Japan*, **17**, 39–47 (1944): *Chem. Abs.*, **44**, 9718 (25th Oct. 1950).
Analyses and results of vulcanization tests of various types of carbon black are given. C. O. C.

Microcrystalline Carbon. G. L. Ruess. *Ciencia e Invest.* (Buenos Aires), **6**, 257–267 (1950): *Chem. Abs.*, **44**, 9762 (10th Nov. 1950).
A review with 15 references of the crystalline structure and size, chemical properties, types of aggregation, and uses of graphite and several commercial carbon blacks. C. O. C.

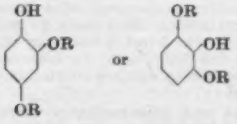
PATENTS

Resorcinol Monoethers as Azo Components in Diazotype Printing. W. H. von Glahn, L. N. Stanley, and General Aniline & Film Corpn. *U.S.P.* 2,516,931.
Compounds of formula—



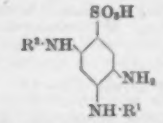
(R = alkyl, *cyclo*alkyl, aryl, aralkyl, which may be substituted by halogen, hydroxy, alkoxy, carboxy, carbalkoxy, carbamyl, sulpho, and amino; X = H, Hal, or an aliphatic radical) have high stability to precoupling and yield sepia images. C. O. C.

Dialkoxyphenols as Diazotype Colour Formers. General Aniline & Film Corpn., W. H. von Glahn, and L. N. Stanley. *B.P.* 646,543.
Compounds of formula—



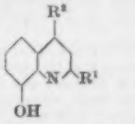
(R = methyl, ethyl, or β-hydroxyethyl) have high stability to precoupling and with suitable diazo compounds yield yellows to sepias. C. O. C.

Derivatives of 4:6-Diaminometanilic Acid as Colour-forming Developers for Phenazonium Dye Images. General Aniline & Film Corpn. and R. C. Gunther. *B.P.* 646,490.
Compounds of formula—



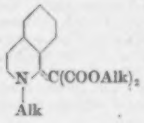
(R^1 and R^2 = alkyl, carboxyalkyl, hydroxyalkyl, aryl, carboxyalkylaryl, carboxyalkoxyaryl, hydroxyalkylaryl, or hydroxyalkoxyaryl, either or both having an aliphatically linked hydroxyl or carboxyl group) used as colour formers for phenazonium dye images do not stain, any excess being readily and completely removed by washing. C. O. C.

Magenta Phenazonium Dyes. General Aniline & Film Corpn. and R. F. Coles. *B.P.* 646,348.
Compounds of formula—

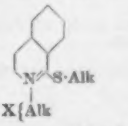


(R^1 = an electronegative group; R^2 = H, COOH, or a carboxyamido (carbamyl) group containing an alkyl chain of > 9 C) used as colour formers in conjunction with a 2:4-diaminoaniline developer yield magenta phenazonium dye images. C. O. C.

1-Dicarbalkoxymethylene-2-alkyl-1:2-dihydro-*iso*quinolines—Intermediates for Carbocyanine and Methin Dyes. F. L. White, L. G. S. Brooker, and Eastman Kodak Co. *U.S.P.* 2,518,512.
Compounds of formula—



are obtained by condensing a compound of formula—



(X = an anion) with one of formula $CH_2(COOAlk)_2$. They can be condensed with quaternary *cyclo*ammonium salts containing a β-arylaminovinyl group to give carbocyanine dyes and with other substances to give other kinds of methin dyes. C. O. C.

Polyacetoacetyl Derivatives of Polyamines as Azo Coupling Components in Diazotype Photoprinting Material. General Aniline & Film Corpn., W. H. von Glahn, and L. N. Stanley. *B.P.* 645,495.
Polyacetoacetyl derivatives of aliphatic polyamines wherein the acetoacetyl groups are attached to amino nitrogen atoms of the polyamines, when used as azo coupling components, yield colours whose covering power markedly surpasses those obtained with monoacetoacetyl derivatives. Used for shading purposes in combination with phloroglucinol, 2:3-dihydroxynaphthalene, or 2:3-dihydroxynaphthalene-6-sulphonic acid, they yield excellent neutral blacks. C. O. C.

1-Amino-4-bromoanthraquinone-2-sulphonic Acid. W. Freudenberg and General Aniline & Film Corpn. *U.S.P.* 2,503,254.
Improved yield of 1-amino-4-bromoanthraquinone-2-sulphonic acid is obtained by preparing the initial aqueous suspension of 1-amino-2-sulphonate by pouring a solution of the sulphonic acid into brine. Thus, all parts being by weight, to a filtered solution of 1-aminoanthraquinone-2-sulphonic acid (75) in water (750) are added 78% sulphuric acid (40) and sodium sulphate (18), and the whole is

diluted to 1750 parts by volume. The resulting solution is added over 30 min. at 10°c. to sodium chloride (153) in water (450). The suspension so formed is brominated in the usual manner. R. K. F.

Metalliferous Azo Dyes. Ciba Ltd. *B.P.* 644,883.

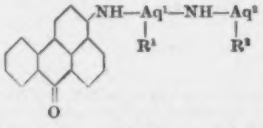
The metallization with simultaneous dealkylation of *o*-hydroxy-*o'*-alkoxyazo compounds is advantageously accomplished in presence of an aliphatic amine containing an OH group, purity of product being superior to that obtained by metallization in presence of ammonia or organic amines free of OH groups. Thus, all parts being by weight, the disazo compound dianisidine→2 mol. H acid (10) is dissolved in water (400) containing diethanolamine (40). A solution of $CuSO_4,5H_2O$ (5) in water (14) containing ammonia (1·36) is then added. After 14 hr. at 80–90°c. the dye is isolated by salting out. It dyes cotton pure greenish blue. E. S.

Yellow and Orange Substantive Disazo Dyes containing Copper. F. P. Reed and I.C.I. Ltd. *B.P.* 644,897.

Mainly orange substantive dyes, whose fastness to light on regenerated cellulose is at the most slightly changed by a resin crease-resisting process, are made by introducing substantially 2 atoms of Cu into each molecule of a disazo dye 4-amino-3-carboxy-1-(4'-methoxy-3'-aminobenzoyl)-anilide→2 mol. of one or more 1-aryl-5-pyrazolones, which contain no diazotizable amino groups and do not have OH and COOH groups *ortho* to one another in the aryl nucleus, and which are so chosen that each contains at least one solubilizing group and that the resulting disazo compound contains either two or three solubilizing groups (COOH or SO_3H) in addition to the COOH group present in the tetrazo compound. An alternative route to the same disazo compounds is to couple with a 1-aryl-5-pyrazolone a diazotized 3-carboxy-1-(4'-methoxy-3'-aminobenzoyl)-anilide containing in the 4-position a group –N:N·P, where P is a suitable 1-aryl-5-pyrazolone. Thus 6-nitro-3-aminobenzoic acid is acylated with 3-nitro-4-methoxybenzoyl chloride, and the resulting nitro compound reduced with iron and ferrous sulphate to the diamine, which is tetrazotized and coupled with 2 mol. of 1-*p*-sulphophenyl-3-methyl-5-pyrazolone. The disazo compound so formed is heated with ammoniacal copper sulphate to give a yellow–orange substantive dye. E. S.

Benzanthrone–Diacridine Vat Dyes. J. Deinet and du Pont. *U.S.P.* 2,505,234.

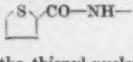
Grey vat dyes are made by caustic alkali fusion of compounds of formula—



(Aq^1 = anthraquinone residue having the two NH groups in α-positions; Aq^2 = anthraquinone residue; R^1 and R^2 = H or CH_3, *ortho* to the NH, and are dissimilar. Thus the condensation product formed by heating together firstly 3-bromobenzanthrone and 1:5-diaminoanthraquinone in nitrobenzene at 170–172°c. in presence of Na_2CO_3 and copper acetate, and then adding 2-bromo-3-methylanthraquinone and heating at 210°c., is stirred with a mixture of KOH and methanol at 145°c. for 2·5 hr. The dye is separated by pouring the melt into water and filtering. R. K. F.

Thienoylaminoanthraquinones. H. R. Lee, C. F. Belcher, and du Pont. *U.S.P.* 2,505,253.

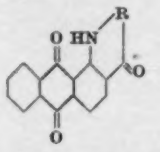
Anthraquinonoid derivatives containing thienoylamino—



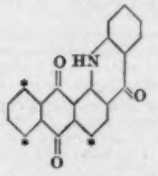
group(s), in which the thienyl nucleus may contain substituents, are dye intermediates and vat dyes. The vat dyes produce deeper shades than the corresponding benzoylamino compounds. They are made by treating aminoanthraquinones with reactive compounds of 2-thienoic acid, e.g. the acid chloride or anhydride. Thus 1-amino-4-hydroxyanthraquinone is heated at 150–155°c. for 2 hr. in nitrobenzene with 2-thienoyl chloride. R. K. F.

Anthraquinone – Acridone – Carbazole Vat Dyes. F. Max, D. I. Randall, and General Aniline & Film Corpn. *U.S.P.* 2,507,479.

Compounds of formula—



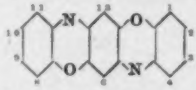
(R = benzene or naphthalene residue fused at the 2':1' positions and containing halogen at position 6'), made by methods described in *U.S.P.* 2,078,996, are condensed with—



(containing one NH_2 group at one of the positions (*), and in some cases substituted in the fused benzene nucleus), and the resulting anthrimides carbazolized, to give violet to blue vat dyes. Thus anthraquinone-2:1-*N*-1':2'-*N*-3':6'-dichlorobenzacridone is heated with anthraquinone-2:1-*N*-1':2'-*N*-4-amino-4'-chlorobenzacridone at 210°c. for 3 hr. in naphthalene containing Na_2CO_3 and copper acetate. After separating, the resulting anthrimide is cyclized by treating in nitrobenzene with $AlCl_3$ at 90–100°c. for 1 hr. R. K. F.

Sulphur Dyes. G. B. Robbins and du Pont. *U.S.P.* 2,504,153.

Red to violet sulphur dyes are prepared by treating a compound containing the triphendioxazine grouping—



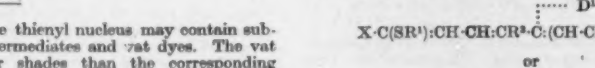
but free of water-solubilizing groups with the complex formed by fusing aluminium chloride with sulphur monochloride. Thus 6:13-dichlorotriphendioxazine (from *o*-anisidine and chloranil followed by cyclizing) is heated at 170°c. with the agent formed by stirring anhyd. aluminium chloride with twice its weight of sulphur monochloride at 80–100°c. The dye is separated by pouring into ice-cold dil. HCl and purified by extracting with aqueous NaOH. R. K. F.

Magnesium Phthalocyanine. J. L. Porter and Kaiser Aluminum & Chemical Corpn. *U.S.P.* 2,502,748.

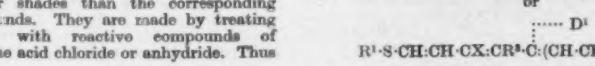
The blue pigment magnesium phthalocyanine is made by heating phthalic anhydride, phthalimide, or phthalamide with a nitrogen compound of magnesium, e.g. the nitride, at about 300°c. Thus finely divided magnesium nitride is mixed with 2 mol. proportions of phthalimide and heated at 280–300°c. until the mass solidifies. The pigment is separated by washing alternately with aqueous alkali and acid. R. K. F.

Cyanine Dyes and Intermediates therefor. F. P. Doyle, J. D. Kendall, and Ilford Ltd. *B.P.* 645,966.

Compounds of formula—



or



(R^1 = alkyl or aralkyl; R^2 = alkyl, hydroxyalkyl, or aralkyl; R^3 = H, alkyl, or aralkyl; X = alkyl or aryl; Y^1 = an acid radical; D^1 = residue of a 5- or 6-membered heterocyclic ring; n = 0 or 1), useful as cyanine dye intermediates, are obtained by interaction of a compound of formula—

$$X{\cdot}C(SR^1)_2{\cdot}CH{:}CH{\cdot}SR^1 \quad \text{or} \quad X{\cdot}C(SR^1){:}CH{\cdot}CH(SR^1)_2$$

with one molecular equivalent of a compound of formula—

$$Y^1\{R^3{\cdot}\overset{\overset{D^1}{\cdots\cdots}}{N}{:}(CH{\cdot}CH)_n{:}C{\cdot}CH_3{\cdot}R^2$$

B.P. 645,967.

Dicarbocyanine dyes are obtained by reaction of the above intermediates with a compound of formula—

$$Y^2\{R^4{\cdot}\overset{\overset{D^2}{\cdots\cdots}}{N}{:}(CH{\cdot}CH)_n{:}C{\cdot}CH_3{\cdot}R^5$$

(R^4 = alkyl, hydroxyalkyl, or aralkyl; R^5 = H, alkyl, or aralkyl; Y^2 = an acid radical; D^2 = residue of a 5- or 6-membered heterocyclic ring).

B.P. 645,968.

The intermediates are treated with not < 2 molecular equivalents of formula—

$$Y^1\{R^1{\cdot}\overset{\overset{D^3}{\cdots\cdots}}{N}{=}{=}{=}C{\cdot}CH_3$$

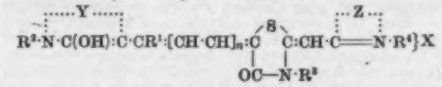
(D^3 = residue of a benzthiazole or benzselenazole ring), preferably in presence of an acid anhydride and a strong organic base to yield symmetrical dicarbocyanine dyes of formula—

$$R^1{\cdot}\overset{\overset{D^3}{\cdots\cdots}}{N}{\cdot}{-}{-}{-}{-}{-}{-}{-}{-}\overset{\overset{D^3}{\cdots\cdots}}{C}{:}CH{\cdot}CH{:}CH{\cdot}CX{:}CH{\cdot}C{=}{=}{=}N{\cdot}R^2\}X^1$$

C. O. C.

Tri- and Tetra-nuclear Cyanine Dyes. T. R. Thompson and General Aniline & Film Corpn. *U.S.P.* 2,518,730.

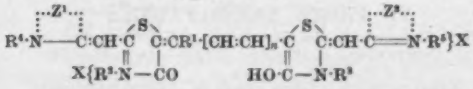
Trinuclear cyanine dyes of formula—



(R^1 = H or Alk, but only Alk when n = 0; R^2 and R^3 = same or different Alk, allyl, aryl, or aralkyl; R^4 = subst. or unsubst. aliphatic, aryl, or aralkyl; n = 0, 1, or 2; X = an acid radical; Y = residue of a 5-membered heterocyclic N-ring system of the type used in *mero*cyanine dyes; Z = residue of a heterocyclic N-nucleus of the type used in cyanine dyes) are obtained in excellent yield and in readily purifiable form by treating a 3-alkyl, 3-aryl, or 3-aralkyl substituted 5-membered ketomethylene heterocyclic compound containing a reactive methylene group adjacent to a keto group with a thiazolone cyanine dye salt intermediate, in presence or absence of a solvent and in presence of a basic condensing agent, either on a steambath or under reflux for 5–20 min.

U.S.P. 2,518,731.

Symmetrical and unsymmetrical tetranuclear cyanine dyes are obtained in excellent yield and in readily purifiable form by treating a thiazolone cyanine dye salt containing a reactive methylene group adjacent to a keto group with a thiazolone cyanine dye salt in the above manner. They have the following general formula—

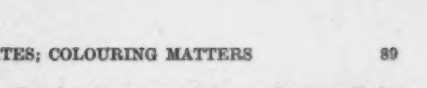


(R^1 = H or Alk, being only Alk when n = 0; R^2 and R^4 = Alk, allyl, Ar, or aralkyl; R^4 and R^5 = lower Alk, lower hydroxyalkyl, lower alkoxyalkyl, aryl of benzene or naphthalene series, or aralkyl; n = 0, 1, or 2; X = an acid radical; Z^1 and Z^2 = atoms necessary to complete heterocyclic nuclei of the type contained in cyanine dyes; at least one of the pairs R^2, R^3 and Z^1, Z^2 are dissimilar.

C. O. C.

***mero*Cyanine Dyes containing a Carboxyalkyl or Sulphoalkyl Group.** R. H. Sprague and Eastman Kodak Co. *U.S.P.* 2,519,001.

Acidic *mero*cyanine dyes of formula—

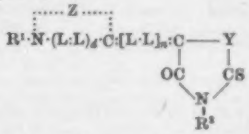


(R^1 = carboxyalkyl or sulphoalkyl; L = methin group; n = 0 or 1; m = 0, 1, 2, or 3; Q^2 = O, S, N(Alk), or N(Ar); R^2 = Alk or Ar; d = 0 or 1; Q^1 = atoms necessary to complete a 5- or 6-membered heterocyclic nucleus; Z = atoms necessary to complete a heterocyclic nucleus) are obtained by condensing a carboxy- or sulpho-alkyl-*cyclo*ammonium quaternary salt, containing in the α or γ position an alkylthio or arylthio group or a halogen atom, with a 5- or 6-membered heterocyclic compound containing a $-COOCH_2-$ group in the heterocyclic ring.

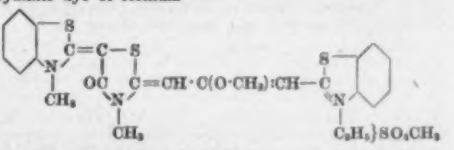
C. O. C.

Methin Dyes. A. E. van Dormael and Gevaert Photo-Producten N.V. *B.P.* 646,137.

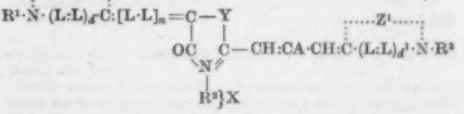
Methin dyes of formula—



(L = a subst. or unsubst. methin group and may be the same or different; d = 0 or 1; n = 0, 1, or 2; R^1 = subst. or unsubst. alkyl; R^2 = subst. or unsubst. alkyl or aryl; Z = atoms necessary to complete a heterocyclic 5- or 6-membered nucleus, which may have a fused-on arylene nucleus; Y = O or S) are obtained by treating a *mero*cyanine dye of formula—



or a corresponding alkylthio quaternary salt with a compound of formula—

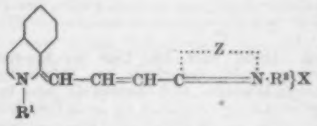


(Z^1 = atoms necessary to complete a 5- or 6-membered heterocyclic nucleus, which may have an arylene nucleus fused on and which may be the same as or different from Z; X = an acid radical; d^1 = 0 or 1; R^3 = subst. or unsubst. alkyl; A = subst. OH).

C. O. C.

Methin Dyes containing an *iso*Quinoline Nucleus. F. L. White, L. G. S. Brooker, and Eastman Kodak Co. *U.S.P.* 2,518,737.

Dyes of formula—

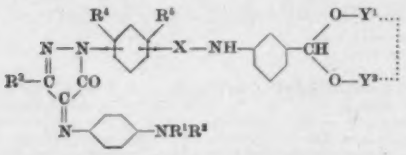


(R^1 and R^2 = Alk; X = an anion; Z = atoms to complete a 5- or 6-membered heterocyclic nucleus) are obtained by condensing *N*-alkyl-1-methyl*iso*quinolinium quaternary salts with *N*-alkyl*cyclo*ammonium quaternary salts or

other intermediates to give carbocyanine or other polymethin dyes having photographic sensitizing properties. C. O. C.

Magenta Azomethin Dyes. E. L. Martin and du Pont. *U.S.P.* 2,518,705.

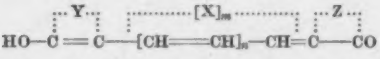
Magenta dyes of formula—



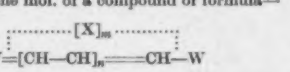
(R^1 and R^2 = C_1–C_4 Alk; R^3 = hydrocarbon radical of 1–10 C; R^4 and R^5 = H, Hal, CH_3, or $CH_3{\cdot}O$; X = CO or SO_2; Y^1 and Y^2 = C_1–C_4 Alk or together may be joined to form a bivalent sat. aliphatic hydrocarbon radical of 2–4 C wherein 2–3 atoms only are in the chain between the two O atoms) are obtained by treating a lower acetal with a *p*-aminodialkylaniline in presence of a mild oxidizing agent under alkaline conditions. C. O. C.

Polymethin Dyes. Gevaert Photo-Producten N.V. *B.P.* 646,123.

Good yields of dyes of formula—



(*n* and *m* = 1 or 2; Y and Z = atoms necessary to complete a carbocyclic or heterocyclic ring, which may have fused-on rings attached to it; X = atoms necessary to complete a carbocyclic or heterocyclic ring with any 2 atoms of the polymethin chain; X, Y, and Z may be the same or different) are obtained by condensing 2 or 3 mol. of a carbocyclic or heterocyclic 5- or 6-membered compound containing a reactive methylene group next to a CO group with one mol. of a compound of formula—



(V = O, >N·Ar, or $(O{\cdot}Alk)_2$; W = OH, ONa, O·Alk, O·CO·Alk, O·CO·Ar, Hal, or subst. NH_2). Thus a purple-red dye is produced by condensing 1 mol. of 4:4′-methenyl-bis-1-phenyl-3-methyl-5-pyrazolone with 1 mol. of 1-phenyl-3-methyl-5-pyrazolone.

B.P. 646,125.

The above dyes are used in photographic filter and anti-halation layers. C. O. C.

Essence d'Orient or Pearl Tincture. F. Buitelaar. *B.P.* 645,803.

Fish, fish scales, swimming bladders, or other silver-white parts of fish and guano are heated for a short time with water or steam at 65–100°c. They are then treated with a water-immiscible liquid of sp. gr. 1·1–1·3 so that the guanine crystals remain in suspension and the mucous substances float to the top, whence they are removed. The resultant suspension of guanine crystals is then brought to the desired sp. gr. by adding a miscible liquid. C. O. C.

Anatase Titanium Dioxide. W. J. Cauwenberg, C. A. Tanner, Jr., and American Cyanamid Co. *U.S.P.* 2,516,548.

Production of a pigment of high tinting strength by hydrolysis of titanium sulphate is described. C. O. C.

Nucleating Agent and its Use in Hydrolysing Titanium Salt Solutions in Production of Titanium Dioxide. C. A. Tanner, Jr., and American Cyanamid Co. *U.S.P.* 2,516,694.

Formulation of Copper Phthalocyanine Finishes. E. C. Botti. (V, this page.)

Diffusion of Dye Solutions. M. Nakagaki. (VIII, p. 93.)

V—PAINTS; ENAMELS; INKS

Elementary Processes in the Drying of Oils. W. Kern. *Farben, Lacke, Anstrichstoffe*, **4**, 242–249 (1950).

Formulation of Copper Phthalocyanine Finishes. E. C. Botti. *Official Digest Paint & Varnish Production Clubs*, No. **305**, 408–417 (1950): *Chem. Abs.*, **44**, 10,349 (10th Nov. 1950).

A crystallization-resistant phthalocyanine blue pigment is now available (du Pont). When used for tinting enamels there is no strength or colour loss. Flocculation of copper phthalocyanine is reduced by use of aromatic rather than aliphatic solvents when grinding, by using long soya-modified alkyds rather than the corresponding linseed alkyds, and by use of a flocculation-resistant lake prepared with Al benzoate. In a laboratory ball mill maximum strength was developed at a pigment : binder ratio of 0·75 : 1·0 by weight. On a laboratory roller mill, maximum strength was developed at a pigment : vehicle ratio of 3 : 7 after 3 passes. C. O. C.

Adsorption of Cobalt Naphthenate by Cellulose Fibres. R. R. Coupe and W. H. Banks. *Research*, **3**, 528–530 (Nov. 1950).

Drying of printing inks is retarded by some types of paper, particularly those which yield hot aqueous extracts of low pH. When solutions of cobalt naphthenate in linseed and olive oils are applied to acidified filter paper, cobalt is irreversibly absorbed, as it is in the case of non-acid paper from olive oil solution. It is apparent that this absorption inhibits the drying of linseed oil. C. O. C.

PATENTS

Printing Ink or Paper Coating and its Application. D. R. Erickson. *U.S.P.* 2,518,607.

A printing ink composed of pigment and a thermo-setting water-insoluble glyceryl phthalate and its alkali-metal salt dispersed in a water-miscible liquid glycol or polyglycol ether is treated immediately after printing with an aqueous solution of a salt of a metal whose phthalate is insoluble in the glycol or polyglycol ether. It is quick setting and does not offset. C. O. C.

Transfer Ink and Carbon Papers produced by its Use. D. A. Newman and Columbia Ribbon & Carbon Manufacturing Co. Inc. *U.S.P.* 2,519,321.

A pigment and/or dye and carnauba wax or a substitute therefor are dispersed in a mixture of non-volatile and volatile liquid vehicles which do not dissolve or disperse the wax when cold. The composition behaves as a printing ink at room temperature and so can be printed on to paper. The resultant coating looks dull and rough, and is heated to coalesce the wax particles, while at the same time the volatile vehicle is evaporated off, leaving a smooth hard smudge-proof carbon paper. C. O. C.

Mildew-resistant Paint. A. J. Lewis and U.S. Secretary of Agriculture. *U.S.P.* 2,517,580.

Addition of 3–7% of CuO on the total weight of paint to an iron oxide–soya-bean oil (2 : 1 parts by weight) paint greatly increases its resistance to mildew and in addition confers faster drying, improved colour retention, decreased dirt retention, and increased durability. C. O. C.

Woven American Materials 9000 Years old — European Paintings aged 15,000 Years. [W. F. Libby and J. R. Arnold.] (VI, p. 92.)

Bleaching of Linseed Oil with Benzoyl Peroxide and the Influence of Certain Antioxidants. P. Colomb. (VII, p. 93.)

VI—FIBRES; YARNS; FABRICS

New Concepts in the Structure of Cellulose and its Derivatives. F. Happey. *J. Textile Inst.*, **41**, T 381–T 403 (Oct. 1950).

The structure of cellulose and its derivatives is discussed in the light of the following considerations— (1) A modified theory of nitration is advanced, in which X-ray photographs of nitrated cellulose do not agree exactly with Mathieu's values, which are corrected accordingly. It is postulated that two crystalline systems, a dinitro and a trinitro, exist in the nitrated fibre. (2) The reasons for (1) are discussed in relation to the penetration of cellulose by acid liquors, in particular during acetylation. (3) A

crystalline secondary acetate is made by hydrolysis of commercial triacetate in solution, and the structure based on isomorphic replacements in the lattice of triacetyl cellulose II. (4) This theory of isomorphic replacements is used to explain, *inter alia*, the two-phase structure in the crystalline nitrocellulose of (1). It is considered that isomorphism may play its most important rôle in the fibrous proteins. J. W. B.

Penetration of Cellulose Fibres. A. J. Stamm and H. Tarkow. *J. Phys. & Colloid Chem.*, **54**, 745–753 (1950): *Chem. Abs.*, **44**, 9145 (10th Oct. 1950).

Pure cellulose and ligno-cellulosic fibres can be directly penetrated only by polar liquids. These liquids, except for a small correction for adsorption compression, add their volume to the volume of the cell walls, indicating that they are not entering existing voids but are forming a solid solution with the fibres. The extent to which a liquid penetrates and swells the fibres seems to be dependent upon its ability to form hydrogen bonds with the OH groups of cellulose and lignin, and also upon the size of the molecules of the liquid. Although in some cases solutions may penetrate the fibres much more slowly than the solvent, they eventually cause greater swelling than either component alone. This enhanced swelling can be explained on the basis of an equilibrium between sorption, solution pressure, and structural resistance. Non-polar liquids, which by themselves do not penetrate fibres, can replace polar liquids already in the fibres except for the unimolecularly held portion of the polar liquid. C. O. C.

Heterogeneous Methanolysis of the Native and Mercerized Cotton Cellulose. R. E. Reeves, L. W. Mazzeno, and C. L. Hoffpauir. *J. Amer. Chem. Soc.*, **72**, 4773–4777 (Oct. 1950).

Methanolysis of cotton cellulose produces two measurable results—introduction of acid-labile methoxyl groups into the insoluble phase and dissolution of part of the cellulosic material into the methanolysis reagent. Looking at the reaction as a whole, the rate of methanolysis smoothly decreases in the region where 0·1–5·0% of the glucose units have been affected. Throughout this region the temperature coefficient for native cotton cellulose remains constant; for mercerized, a lower, essentially constant value was observed. Apparently the rate-controlling step in methanolysis involves in a single step the rupture of secondary as well as primary valency forces. The available data are compatible neither with the concept of reaction in an amorphous region nor with relatively few acid-sensitive linkages, but they are compatible with an initially large crystalline surface, diminishing strongly as the surface is reduced by coalescence of crystalline areas when internal tensions relax owing to reaction within the fibre. C. O. C.

Application of the Kozeny Equation to Consolidated Porous Media. J. E. Adamson. *Nature*, **166**, 314–315 (19th Aug. 1950).

A study of the flow of CCl_4 and petroleum ether through long wool fibres, packed randomly in a spherical cell and oriented parallel to the axis of a cylindrical cell, show that in the porosity range 0·82–0·86 the data are independent of the type of packing and conform to the equation—

$$\log k = \text{const} - b \log \frac{1}{1-\varepsilon}$$

where k is the numerical constant in the Kozeny equation and ε is the porosity. This equation is then used to calculate the k function for water, which cannot be determined experimentally because of unknown swelling effects. J. W. B.

Frictional Properties of Wool Fibres. K. R. Makinson and G. King. *J. Textile Inst.*, **41**, T 407–T 410 (Oct. 1950).

The nature of friction in general, dependence of friction on regain, dependence of D.F.E.* on swelling, and dependence of μ on pressure are discussed by Makinson in a criticism of a paper by King (*ibid.*, **41**, T 135 (April 1950): J.S.D.C., **66**, 495 (Sept. 1950)), who replies to the criticisms. J. W. B.

* Differential frictional effect.

Recent Advances in Knowledge of Wool Structure. H. Lindley. *Research*, **3**, 509–513 (Nov. 1950).

A review, with 51 references. C. O. C.

Action of Alkali on the Epicuticle of Wool. G. Lagermalm and B. Philip. *Text. Research J.*, **20**, 668–670 (Oct. 1950).

The epicuticle of wool can be isolated in a short time by treating the fibre with 1% sodium sulphide at 60°C. for 24 hr., and then with a solution of the same concentration at room temperature for about 1 week. Electron-micrographs are given showing the degree of penetration and disintegration of the epicuticle caused by dilute sodium sulphide or caustic potash. The thickness of the epicuticle varied from 50 to 250 A. The importance of damage to the epicuticle in relation to dyeing phenomena and tests for wool damage is discussed. P. C.

Composition of the Fibroin and Sericin of Silks of Various Origins. J. Roche, R. Michel, and M. Bozzi-Tichadou. *Compt. rend. Soc. biol.*, **144**, 100–102 (1950): *Chem. Abs.*, **44**, 10,001 (10th Nov. 1950).

Bombyx mori silk from Italy, France, Japan, Persia, and various parts of China showed small but significant differences in glycine, alanine, serine, and tyrosine contents of the fibroin and in the glycine, serine, and tyrosine contents of the sericin. Fibroin of Chinese tussah silk spun by *Phaeolamia cynthia* contained 22·1% glycine, 18·3–19·0% alanine, 15·1–15·6% serine, and 8·7–9·7% tyrosine. Its composition is quite different from that of *Bombyx mori* silk. C. O. C.

State of Solution in Emulsion-xanthated Viscoses. F. Gärtner and O. Samuelson. *Svensk Papperstidning*, **53**, 635–637 (31st Oct. 1950).

Various types of cellulose were shaken with CS_2 and NaOH solutions of different concentrations, and the resulting cellulose xanthate solutions diluted to equal concentrations of cellulose and NaOH. A technical viscose was also diluted to the same concentration. It was shown that the viscosity was practically independent of the original concentration. This was accounted for by the xanthate being in molecular dispersion and was confirmed by ultracentrifuging. S. V. S.

Combined Calcium in Dissolved Pulps and its Behaviour in the Viscose Process I—Influence of Alkalization. T. Kleinert and W. Wincor. *Svensk Papperstidning*, **53**, 638–643 (31st Oct. 1950).

The absorption of Ca by cellulose from dilute solutions containing Ca ions is an ionic reaction with the COOH groups in the cellulose. Most of the Ca diffuses out with the hemicellulose during mercerization with NaOH, and the Ca–hemicellulose complex can be separated from the liquor by dialysis. The COOH content of spruce sulphite is twice that of beech sulphite pulp. S. V. S.

Study of the Affinity of Saponified Cellulose Acetates for Direct Dyes. J. Rosset and R. Paris. *Bull. Soc. chim. France*, 334–340 (1950): *Chem. Abs.*, **44**, 9671 (25th Oct. 1950).

Microscopic examination of commercial cellulose acetate, saponified with NaOH and coloured with a direct dye, revealed the existence of an intermediate layer, coloured much deeper than the external layers composed of completely deacylated cellulose. This indicated the presence of a series of partly saponified acetates having greater affinity for dyes than has the completely deacylated cellulose. This was confirmed by examining the affinity for direct dyes of a series of acetates saponified homogeneously with NaOH to various degrees. The curve of the variation in affinity for direct dyes as a function of the acetyl content of deacetylated samples passed through a flat maximum which corresponded to samples of 29–30% acetyl content. This maximum appeared therefore to be in the neighbourhood of a monoacetate (theoretical acetic acid content 29·43%). The affinity of such acetates for direct dyes is twice or thrice that of a completely deacetylated cellulose. C. O. C.

Properties of Glass Fibres as a Function of their Production. G. Keppeler and R. Jankowski. *Glastech. Ber.*, **23**, 196–203 (1950): *Chem. Abs.*, **44**, 9649 (25th Oct. 1950).

Glass fibres can be produced by drawing, centrifuging, or blowing methods. It is not yet possible to establish a clear relation between chemical composition and the corrosion resistivity of spun glass, but the method of production has a decided effect on the physical and chemical properties of the fibre. C. O. C.

Glass Fibres for Textiles. G. Satlow. *Glastech. Ber.*, **23**, 89–99 (1950): *Chem. Abs.*, **44**, 9649 (25th Oct. 1950).
Production methods affect the fibre diameter and the tensile strength, evidently by the effect of water on the fibre surface. Theoretical aspects of the bearing of glass structure on the fibre strength are discussed. Glass fibres produced by the blowing processes are distinctly more brittle than those produced by drawing either from nozzles or spun from rods. The use of glass fibres is discussed. There are 45 references. C. O. C.

Glass Fibres for Textiles. P. A. Koch. *Glastech. Ber.*, **22**, 226–228 (1949): *Chem. Abs.*, **44**, 9650 (25th Oct. 1950).
A tabular classification of glass filaments, yarns and fabrics, production methods, composition of the glasses used, mechanical and chemical properties, production in various countries, and literature. C. O. C.

Woven American Materials 9000 Years old — European Paintings aged 15,000 Years. [W. F. Libby and J. R. Arnold.] *Science News Letter*, **58**, 243, 244 (14th Oct. 1950).
Woven rope sandals found in a lava-covered Oregon (U.S.A.) cave as measured by their ^{14}C content are 9000 years old. The paintings in the Lascaux cave in Dordogne, France, are apparently 15,000 years old, as dated by the charcoal found there. C. O. C.

PATENTS

Viscose Rayon. B. W. Collins and American Viscose Corpn. *U.S.P.* 2,519,227.
Fouling of the spinnerets is avoided and more level filaments are obtained by adding a stable, surface-active non-ionogenic acetal of a polyethylene glycol containing a hydrocarbon chain of $> 7C$ and > 7 oxyethylene units per mol. to the aqueous acid coagulating bath. C. O. C.

Crimped Viscose Rayon. H. D. Merion, W. A. Sisson, and American Viscose Corpn. *U.S.P.* 2,517,694.

Incorporating Opacifying Agents in Viscose Spinning Solutions. K. R. Gray and Rayonier Inc. *U.S.P.* 2,516,113.

High-tenacity Viscose Rayon. W. A. Hare, F. K. Signaigo, and du Pont. *U.S.P.* 2,516,316.
Viscose is extruded into a bath containing a borate in amount equivalent to not $< 5\%$ of borax, the bath being kept so that it precipitates the viscose without converting it to regenerated cellulose. The water-soluble cellulose xanthate filaments are then stretched, after which they are converted to regenerated cellulose by any suitable method. C. O. C.

Dispersion of Keratinous Materials—Man-made Fibres from Feathers and other Keratinous Materials. C. B. Jones, D. K. Mecham, and U.S. Secretary of Agriculture. *U.S.P.* 2,517,572.
Keratinous materials are heated at not $> 100°C$. in a neutral aqueous solution containing an alkali-metal salt of an alkarylsulphonate or of an alkyl sulphate and a sulphur-containing, disulphide-splitting reducing agent, e.g. monoethylene thioglycol, thioglycollic acid, or sodium bisulphite. This disperses the keratin with less degradation than by hitherto known methods. The keratin may be recovered in a form similar to the original in respect of its composition, isoelectric point, solubility, and other properties. The process may be used for producing fibres from feathers, horns, hoofs, wool, etc. C. O. C.

Hardening Casein Fibres. Courtaulds Ltd., L. E. Hodges, C. L. Knight, W. Walker, and R. L. Wormell. *B.P.* 645,390.
Fibres of improved resistance to boiling water and dilute acids are produced by hardening freshly spun threads at 35–60°C. in a bath containing 500–800 g. sodium bisulphate and 5–15 g. formaldehyde per litre. W. G. C.

Calcium Alginate Monofil. Courtaulds Ltd. and E. E. Tallis. *B.P.* 645,243.
Uniform monofil of circular cross-section is obtained by extruding a solution of a water-soluble salt of a polyuronic acid, e.g. sodium alginate, through a single-hole jet into a coagulating bath containing a metal salt, e.g. $CaCl_2$, which forms an insoluble polyuronate, maintaining the monofil in the bath till completely set, drying below 40°C. in a strain-free condition, rewetting, and finally drying while preventing longitudinal shrinkage. W. G. C.

Artificial Wool from Nylon Fibres. B. Graham and du Pont. *U.S.P.* 2,516,562.
Nylon having wool-like crimp, elongation, and dye receptivity is obtained by heating oriented nylon, which has been rendered insoluble in solvents in which it was initially soluble, to 10–50°C. below its softening point until the filaments have shrunk at least 20% and preferably at least 50% of their original oriented length. C. O. C.

Spinning Saran Filaments. Firestone Tire & Rubber Co. and T. W. Stedman. *B.P.* 645,275.
Fine filaments of a vinylidene chloride polymer or copolymer are obtained by extruding the molten polymer into a chamber 30–50 ft. high at 200°F. and allowing the fibre to stretch under its own weight. W. G. C.

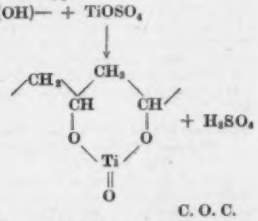
Cyanoaminoacetonitriles as Solvents for Acrylonitrile Polymers in making Fibres, Films, etc. A. Cresswell and American Cyanamid Co. *U.S.P.* 2,517,544.
Compounds of formula $CN{\cdot}R{\cdot}N(CH_2{\cdot}CN){\cdot}R{\cdot}CN$ (R = an alkylene radical of < 5 C and may be the same or different) are solvents or plasticizers for homopolymeric acrylonitriles. Mixtures of the two may be used for making filaments, films, etc. C. O. C.

Fibres from Poly-1:2:4-triazole. British Celanese Ltd., J. W. Fisher, E. W. Wheatley, and H. Bates. *B.P.* 645,907.
Modification of *B.P.* 613,497 (cf. J.S.D.C., **65**, 256 (May 1949)). Spinning is greatly facilitated if the formaldehyde treatment is carried out by adding the formaldehyde to the coagulating bath. C. O. C.

Polyethylene Terephthalate. E. F. Casassa and du Pont. *U.S.P.* 2,518,283.
Zinc borate is an excellent catalyst for the formation of polyethylene terephthalate from ethylene glycol and dimethyl terephthalate. C. O. C.

Films and Fibres of Titanated Polyvinyl Alcohol. F. K. Signaigo and du Pont. *U.S.P.* 2,518,193.
Treatment with quadrivalent titanium salts so as to introduce 1–2% by weight of titanium renders polyvinyl alcohol completely insoluble in boiling water and also confers improved dry strength and greater dimensional stability to films and fibres of polyvinyl alcohol. As films of polyvinyl alcohol containing 25% of titanium are still transparent, a reaction of the type—

$$—CH_2{\cdot}CH(OH){\cdot}CH_2{\cdot}CH(OH)— + TiOSO_4$$



is indicated. C. O. C.

Films, Fibres, Coatings, etc. of Polymers containing both Primary and Secondary Hydroxyl Groups. R. M. Joyce, Jr., and du Pont. *U.S.P.* 2,518,440.
Polymers containing several $–CH_2{\cdot}CH{\cdot}CH(OH){\cdot}CH_2OH$ units are obtained by hydrolysing polymeric vinylethylene carbonate by heating it in aqueous alkali at 50–110°C. C. O. C.

Differentially Coloured Yarns or Fabrics. British Celanese Ltd. *B.P.* 645,148.
When staple-fibre yarns, having twist which varies along their length but does not exceed 25 p.p.in., are dyed, the portions of lower twist dye deeper than those of higher twist. C. O. C.

Films and Fibres of Polymeric Boronamides. R. W. Upson and du Pont. *U.S.P.* 2,517,944.
Treating a boronic acid with an organic compound containing several separate NCO or NCS groups yields polyboronamides or their derivatives. The products all contain in the polymer chain a number of $>N{\cdot}BR{\cdot}N<$ groups (R = a univalent organic radical). They are usually white solids of high softening point, soluble in phenol and in some cases in formic acid, benzene, and ether. They can be formed into films and fibres by pressing or extrusion from solution, and many of them can be cold-drawn. C. O. C.

Films and Fibres of Polymeric Organosilanol-Boronic Acid Reaction Products. R. W. Upson and du Pont. *U.S.P.* 2,517,945.

Organo-inorganic polymers are obtained by treating a polyhydric organosilanol with a boronic acid. Thus the polymers formed from organosilanediols and boronic acids have recurring structural units of probable formula $-SiR^1R^2\cdot O\cdot BR^3\cdot O-$ (R^1, R^2, and R^3 = same or different univalent organic radicals) and are soluble in organic solvents. They can be extruded as fibres at high temperatures, or their solutions can be used for making fibres or films. C. O. C.

VII—DESIZING; SCOURING; CARBONIZING; BLEACHING

Studies on Foams. V—Effect of Electrolytes on Triphenylmethane Dye Solutions. M. Nakagaki. *Bull. Chem. Soc. Japan*, **23**, 102–104 (Aug. 1950).

The addition of NaCl to solutions of Crystal Violet and Brilliant Green causes surface tension to decrease and foam formation to show a maximum, while additions of HCl, and also of NaOH, produce an increase of surface tension with decrease of pH and also a maximum of foam formation at pH ~ 2. These results are explained by a change of surface activity of the dye ion and the displacement of the micelle–ion equilibrium. H. H. H.

Scouring of Wool. M. Robinet. *Teintex*, **15**, 503–517 (Nov. 1950).

A review of wool scouring with special reference to factors controlling the process, such as water, alkali, detergents, and electrolytes. A laboratory method for assessing the value of detergents is described which gives a satisfactory guide for bulk working. B. K.

Milling Wool–Nylon Goods—Covered Finish on a Prunelle Weave Men's Summer Suiting. Anon. *Dyer*, **104**, 309–311 (8th and 22nd Sept. 1950).

Scouring is effected with potash soaps, and using cross-drafting or running through spouts to reduce the width. After rinsing and hydroextracting, the piece or two pieces together are milled with the machine trough as full as possible, e.g. by using four drafts. Milling is performed in two or three stages, under-soaping slightly with 7–10% soda soap soln. Care is essential to avoid mill-rigging and differential drying between nylon and wool. Finally the cloth is scoured, rinsed, hydroextracted, dried, brushed, double-blown, damped, pressed, and if necessary lightly steamed. J. W. B.

Foam Method for Degumming Raw Silk. F. Bryant. *Text. Research J.*, **20**, 735–736 (Oct. 1950).

A foam method for degumming silk is described which is applied in three stages—(*a*) a plasticization bath containing sodium hexametaphosphate, potassium carbonate, and sodium bicarbonate, in which the silk is treated for 10 min. at 80°C.; (*b*) the foam bath containing sulphated cetyl alcohol, potassium carbonate, and sodium bicarbonate, the time of treatment being 20 min.; and (*c*) a warm rinse (10 min. at 60–70°C.) in water containing the two alkali carbonates used in the previous stages. No loss of strength is suffered by the yarn, which has a clean appearance with little hairiness. The time involved is less than that of conventional methods, but the method may be limited in its application to yarns other than raw silk P. C.

Bleaching of Linseed Oil with Benzoyl Peroxide and the Influence of Certain Antioxidants. P. Colomb. *Ind. Vernice* (Milan), **3**, 220–225 (1949): *Chem. Abs.*, **44**, 9695 (25th Oct. 1950).

PATENTS

Hypochlorite Bleaching of Ground Wood. D. O. Adams, G. B. Hughey, and West Virginia Pulp & Paper Co. *U.S.P.* 2,516,634.

Ground wood rich in tannin and colouring matter can be brought to a brightness equal to that of hypochlorite-bleached ground spruce wood by first extracting the tannin, etc. with dil. aq. caustic alkali below b.p. and then treating with alkaline hypochlorite solution containing not > 15% available Cl on the weight of the dry ground wood. C. O. C.

Bleaching Viscose Rayon. Courtaulds Ltd., J. H. Givens, and L. Rose. *B.P.* 645,969.

Viscose rayon produced by a continuous spinning process can be bleached by treating with an agent which will bleach the thread but will be destroyed by reaction with impurities present, e.g. carbon disulphide, and by the rapid heating on the drying reel without the necessity of a souring, antichlor, or washing treatment, which is usually considered essential. The bleaching solution, e.g. dilute sodium hypochlorite, may contain an alkali to neutralize the acid products formed by the action of the bleach on the impure thread. W. G. C.

VIII—DYEING

Diffusion of Dye Solutions. M. Nakagaki. *Bull. Soc. Chem. Japan*, **23**, 104–107 (Aug. 1950).

The apparent diffusion coefficient of Congo Red in water, as obtained by the Auerbach–Ostwald method, changes with concentration, and by solving Fick's equation on the assumption that it is a function of concentration, recalculation of this apparent to the differential diffusion coefficient has been effected. From the value of the latter, extrapolated to infinite dilution, the particle radius of Congo Red has been calculated by means of the Einstein–Sutherland equation. The particle weight and degree of association are obtained on the assumption that the particle is spherical and not hydrated. The diffusion coefficients thus obtained for Congo Red solutions containing various concentrations of sodium chloride agree well with published data. Particle size increases gradually with increase of salt concentration, but no decrease is observed with a small addition of electrolyte. H. H. H.

Acidic Properties of Cotton Cellulose and Derived Oxycelluloses. VII—Ion-exchange Reactions with Basic Dyes. G. F. Davidson. *J. Textile Inst.*, **41**, T 361–T 380 (Oct. 1950).

The affinities of the cations of a number of basic dyes for the carboxyl groups of acidic oxycelluloses are compared (1) by dyeing in competition with varying quantities of Na, K, or other dye cation in the solution and (2) by adsorbing the dyes on columns of acidic oxycellulose and comparing the volumes of buffered NaCl solutions having different Na ion concentrations that are required to effect removal of dye by elution. Wide differences in affinity occur between the dyes, substantially similar orders of affinity being found by both methods. The exchange reaction does not obey the law of mass action, but can be expressed by the equation $R = Kr^p$, where R and r are ratios of the concentrations of competing cations in the cellulose and solution phases respectively, K is a constant, and p a constant < 1. J. W. B.

Application of Vat Colours to Nylon at Normal Temperatures. T. Carter, J. L. Neal, and R. N. Westmoreland. *Amer. Dyestuff Rep.*, **39**, P 773–P 776 (13th Nov. 1950).

Nylon is treated at 190°F. in a 1–5% solution of tannic acid, which when on the fibre is fast to treatment in a blank vat. Subsequent vat dyeings are greatly improved in fastness to light, washing, and rubbing, though they are not so fast as on cotton. Oxidation of the leuco vat dye is best effected by a hot acid solution of sodium chlorite. Fibre cross-sections show a surface layer of deeper colour, and it is suggested that a thin shell of larger dye particles confers greater resistance to light than in the absence of such a shell. J. W. B.

Dyeing of Rhovyl. M. Rampin. *Teintex*, **15**, 519–523 (Nov. 1950).

Rhovyl is a polyvinyl chloride fibre which can be dyed with dispersed acetate dyes, preferably with the addition of a swelling agent such as Solvent F (Francolor), Swelling Agent R3 (Ciba), or Swelling Agent ACS (Rhodiacéta). The quantity of swelling agent used (x ml./litre) depends on the liquor ratio L—

$$x = \sqrt{(1000/L)}$$

for Swelling Agent ACS. The dyebath is set at 45°C. with 0·2 g. of a sulphated fatty alcohol per litre, in which the swelling agent is dissolved, followed by the emulsified dye. The material is entered at 45°C., the temp. raised to 55°C. in 30 min., and dyeing continued for 1 hr. at this temp. Fastness to rubbing is obtained by an aftertreatment with 0·2–0·5 g. of an ethylene oxide–lauric acid condensate per

litre at 30–45°C. Swelling Agent ACS is said to have no deleterious effect on silk, nylon, or wool, and acetate rayon is unaffected up to a concn. of 5 ml./litre, which is well below that which is likely to be used in dyeing unions of acetate rayon and Rhovyl. B. K.

Colouring of Foodstuffs. L. Görnhardt. *Deutsch. Lebensm.-Rundschau*, **44**, 197 (1948): *Chem. Abs.*, **44**, 10,191 (10th Nov. 1950).

General considerations governing the choice of a suitable colouring matter, pH changes, denaturation of proteins, etc. are briefly reviewed. C. O. C.

PATENTS

Wool Dyeing. D. R. Lemin, I. D. Rattee, and I.C.I. Ltd. *B.P.* 645,594.

Acid-milling dyes give surprisingly level dyeings on wool when they are applied from a neutral bath in presence of a neutral inorganic salt and a neutral salt of an aromatic sulphonic acid, preferably a naphthalenedisulphonic acid. C. O. C.

Dyeing Fabrics containing Cellulose Acetate Staple Fibre. British Celanese Ltd. *B.P.* 645,987.

Modification of *B.P.* 583,349 (J.S.D.C., **63**, 146 (1947)). The unscoured fabric is impregnated with an aqueous alcoholic solution of the dye containing an inorganic thiocyanate and then scoured. Level dyeings having no overdyed surface fibres are obtained. C O C.

Dyeing Cellulose Acetate with Acid Dyes. J. A. Woodruff and American Viscose Corpn. *U.S.P.* 2,517,751.

Addition of 1·6% by weight of resorcinol, phloroglucinol, or *cyclo*hexanol to aqueous solutions of acid dyes enables the amount of alcoholic or acid primary assistant (mixture of organic and inorganic acids) needed for the dyebath to be greatly reduced. C. O. C.

Dyeing Cellulose Derivatives in presence of Inorganic Thiocyanates and Organic Acids. G. W. Seymour, G. C. Ward, and Celanese Corpn. of America. *U.S.P.* 2,518,644.

Deep level dyeings of unusual resistance to light and acid fading are obtained very rapidly on cellulose acetate or other organic derivative of cellulose by impregnation with an acid and/or direct cotton and/or acetate rayon dye in an aqueous bath containing not $<$ 20% by weight of a lower aliphatic acid and 3–10% of a thiocyanate, preferably sodium thiocyanate. Dyeing is effected in a few seconds, and the materials may be washed or scoured immediately after dyeing without any intermediate drying, so that the process is suitable for continuous dyeing. C. O. C.

Dyeing Cellulose Esters with Reduced Vat Dyes in Alcoholic Solution. E. R. Laughlin, R. W. Foulk, and du Pont. *U.S.P.* 2,518,153.

Cellulose acetate and other cellulose esters may be dyed continuously with all types of vat dyes and without saponifying the cellulose ester by padding it for not $>$ 10 sec. with an aqueous alkaline solution of the leuco dye, the solution also containing 30–60% of alcohol. For each gal. (U.S.) of dye liquor the alkali should not be more than the equivalent of 2·0 oz. KOH and there must also be 0·1–4·0 oz. wetting agent, 0·25–4·0 oz. dispersing agent, and 0·25–4·0 oz. ethylene glycol, thioethylene glycol, or glycerol. The dye liquor is kept at 110–150°F. Immediately after padding, the material is passed into an aqueous solution of alkalinity below that at which the cellulose ester is saponified, and then the leuco dye is oxidized. C. O. C.

Colouring Walnut Sapwood with Quinol. E. Farber and American Walnut Manufacturers' Assocn. Inc. *U.S.P.* 2,517,296.

Walnut sapwood is given throughout the colour of walnut heartwood by immersing it for 2–60 hr. in a 0·2–3·0% aqueous solution of quinol at pH 2–5 and 70–90°C., and then treating the impregnated wood with ammonia vapour. C. O. C.

Colouring Aluminium or its Alloys. United Anodizing Ltd. and L. G. Tottle. *B.P.* 645,443.

A brown or bronze finish is produced on aluminium by anodizing it, then precipitating ferric hydroxide within the coating, and finally toning the colour by treatment with gallic, pyrogallic, or like organic acid. C. O. C.

Studies on Foams. V—Effect of Electrolytes on Triphenylmethane Dye Solutions. M. Nakagaki. (VII, p. 93.)

IX—PRINTING

PATENTS

Leuco Vat Dye Sulphuric Ester Printing Compositions. A. Topham and I.C.I. Ltd. *B.P.* 644,819.

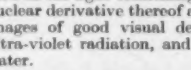
Alkali-metal salts of sulphuric esters of leuco vat dyes are applied in printing pastes in the presence of a compound containing SO_3H and an *iso*thiourea, substituted thiourea, alkylthioiminazoline, or aralkylthioiminazoline group, to give prints of improved strength and brightness. Thus, all parts being by weight, strong orange prints are obtained on cotton by using a preparation consisting of 25% leuco dibromoanthanthrone sulphuric ester paste (10), urea (10), 2-benzylthioiminazoline-*m*-sulphonic acid (5) in water (12), starch–tragacanth thickening (60), and 30% sodium nitrite solution (3).

B.P. 644,904.

Similar preparations contain instead of an *iso*thiourea, etc. derivative a compound containing SO_3H and an amidine, substituted amidine, or 2-aryliminazoline group, e.g. benzamidine-*m*-sulphonic acid. R K F

***N*-Monoalkyl- and *N*-Hydroxyalkyl-*p*-diazoanilines as Light-sensitizing Components in Diazotype Layers.** General Aniline & Film Corpn., W. H. von Glahn, and L. N. Stanley. *B.P.* 646,444.

Compounds of formula—



(R = methyl, ethyl, propyl, butyl, or β-hydroxyethyl) used as the light-sensitizing component and resorcinol or a nuclear derivative thereof as the coupling component yield images of good visual density, outstanding opacity to ultra-violet radiation, and superior fastness to light and water. C. O. C.

Integral Masking of Photographic Silver Halide Emulsions with Azo-substituted Coupling Components. General Aniline & Film Corpn., N. Heimbach, and H. Morreall, *Jr.* *B.P.* 646,367.

Lumazines and Alloxazines as Catalysts in Colour Photography Dye Bleach Baths. F. W. H. Mueller and General Aniline & Film Corpn. *U.S.P.* 2,518,710.

Polyacetoacetyl Derivatives of Polyamines as Azo Coupling Components in Diazotype Photoprinting Material. General Aniline & Film Corpn., W. H. von Glahn, and L. N. Stanley. (IV, p. 87.)

X—SIZING AND FINISHING

Exchange of Radioactive Zinc between Cellulose and Sodium Hydroxide–Sodium Zincate Solutions. K. Borgin and A. J. Stamm. *J. Phys. & Colloid Chem.*, **54**, 772–777 (1950): *Chem. Abs.*, **44**, 8740 (10th Oct. 1950).

Addition of sodium zincate greatly increases the swelling and solvent power of NaOH for cellulose, either by physical adsorption of the Zn complex or by chemical reaction with the cellulose. Radioactive ^{65}Zn in the form of sodium zincate dissolved in conc. NaOH can be rapidly removed by exchange from cotton into an inactive solution of identical strength or into a more conc. soln. counter to the inward diffusion under a concentration gradient. If compound formation does occur, the reaction must be more rapidly reversible than the exchange and the diffusion. C. O. C.

Effect of Urea–Formaldehyde Treatment on the Photochemical Discoloration of Bleached Jute. H. J. Callow. *J. Textile Inst.*, **41**, T 404–T 406 (Oct. 1950).

Reactive phenolic or enolic groups in the lignin of bleached jute are first blocked by methylation with diazomethane, and urea–formaldehyde is then condensed within the samples. No additional effect is found on the subsequent photochemical discoloration, and it is inferred that the inhibiting action of urea–formaldehyde on the discoloration of bleached jute is bound up with the photochemical reactions of the lignin. Some permanent damage is caused by the resin treatment. J. W. B.

Crease Resistance of Wool Cloths—Its Relationship to Scouring and Milling. Anon. *Wool Record*, **78**, 1571, 1572, 1575 (16th Nov. 1950).

A discussion of the causes of rigging, creasing, marking, and bursting and the relationship between these faults and the resistance to creasing of the cloth. C. O. C.

Preservative Treatments for Cloth Nursery-bed Covers, W. E. McQuilkin. *J. Forestry*, **48**, 351–353 (1950): *Chem. Abs.*, **44**, 9609 (25th Oct. 1950).

Cotton netting was given good preservation by treatment with lead acetate–potassium dichromate, copper naphthenate–asphalt–bentonite, quercitron, copper naphthenate–asphalt in naphtha, and fustic. No preservative action was shown by acacia cutch, osage orange extract, soap–cadmium chloride, or Nuodex (a commercial product containing copper naphthenate). C. O. C.

Antimycin A, an Antibiotic with Insecticidal and Miticidal Properties. G. S. Kido and E. Spyhalski. *Science*, **112**, 172–173 (1950): *J. Textile Inst.*, **41**, A 500 (Oct. 1950).

Initial trials have shown that antimycin A (which appears to be an optically active, nitrogenous phenol) causes mortality to some insects by ingestion rather than by contact action. On wool fabric it gives protection against attack by the black carpet beetle (*Attagenus piceus* Oliv.), but fails to give protection against the larvae of the common clothes moth (*Tineola biselliella* Hum.). C. J. W. H.

Treatment of Nylon Webbing to increase Resistance to Abrasion. C. A. Willis. ORR 391/50* (PB 98,652).

Polyvinylbutyral as a 60% aqueous dispersion is better than a 40% aqueous dispersion of polystyrene or an aqueous dispersion of Methacrol-NH for preventing fraying, fuzzing, and abrasion of nylon parachute harness webbing. The treated material lost little or no tensile strength after being abraded 10,000 strokes on each side. C. O. C.

* Photocopies available from T.I.D.U., Board of Trade, Lacon House, Theobalds Road, London W.C.1, or (under PB No.) from Office of Technical Services, Department of Commerce, Washington D.C.—see J.S.D.C., **66**, 53 (Jan. 1950).

PATENTS

Chemically Modified Wool by Use of β-Propiolactone. H. W. Jones, H. P. Lundgren, and U.S. Secretary of Agriculture. *U.S.P.* 2,517,573.

Wool treated with β-propiolactone dissolved in an organic solvent or as vapour is chemically modified, the difference in properties between it and untreated wool depending upon the amount of β-propiolactone used. The treated wool is softer, whiter, more lustrous, and less crimpy, and felts more rapidly than untreated wool. Felts made from it have a greater tensile strength than those prepared from untreated wool. C. O. C.

Saponification of Cellulose Acetate Rayon. British Celanese Ltd. *B.P.* 645,761.

Material which despite its relatively high acetyl value has affinity for and dyes evenly with both direct cotton and acetate rayon dyes is obtained by saponifying acetate rayon of $> 56\%$ acetyl value so as to reduce the acetyl value to 53–55%. The saponification is preferably effected with 1–5% aq. Na_2CO_3 at 80–100°C. C. O. C.

Improving the Resistance of Cellulose Esters to Degradation by Sunlight and Ultra-violet Radiation. Courtaulds Ltd., W. G. Cameron, and L. F. H. Breens. *B.P.* 645,392.

An alkyl gallate, e.g. 10% by wt. of ethyl gallate, is incorporated into the cellulose ester. C. O. C.

Animalizing Cellulose Acetate. T. S. Gardner and Eastman Kodak Co. *U.S.P.* 2,518,676.

Cellulose acetate or similar cellulose esters of lower aliphatic acids are given affinity for wool dyes by treatment with ethyleneimine at 50–150°C. for 2–6 hr. to convert it to a β-aminoethyl cellulose ester. C. O. C.

Batting or Padding from Carded Webs. British Rubber Producers' Research Assocn. and C. M. Blow. *B.P.* 644,648.

Batting or padding material of improved strength and stability is obtained by exposing the carded web or sliver as it emerges from the carding machine to a spray or mist of dilute stabilized rubber latex insufficient to produce a continuous film. On passage through a drying zone, bonding is effected between adjoining fibres. A multiply effect is obtained by superimposing successive laminae on each other, preferably before drying. G. E. K.

Size for Crêpe Yarns. R. R. Sitzler, R. H. Balch, and Celanese Corpn. of America. *U.S.P.* 2,516,267.

Use of an aqueous solution of a water-soluble lower fatty acid ester of cellulose and urea enables the amount of twist in acetate rayon crêpe yarns to be reduced without decreasing the crêpe effect in fabrics woven from such yarns. C. O. C.

Rendering Fabrics Water-repellent. Dow Corning Corpn. *B.P.* 645,768.

The fabric is wetted with an aqueous emulsion of a siloxane polymer more than half of whose siloxane units are of the type $-SiH(CH_3)\cdot O-$. The emulsion contains an emulsifying agent which decomposes when the fabric is dried and subsequently baked above 100°C. C. O. C.

Methylsiloxanes as Water-repellent Finishing Agents. Société des Usines Chimiques Rhône-Poulenc. *B.P.* 645,389.

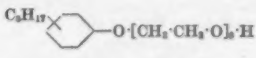
Textiles can be waterproofed by treating them with a solution of a methylsilyl acetate in an organic solvent and then hydrolysing the acetate in the fibre, e.g. with water vapour, to yield a methylsiloxane. This method has the advantage over the use of chlorosilanes that no tendering of the textiles can be caused. C. O. C.

Rendering Regenerated Cellulose Water-repellent. M. M. Cruz, Jr., and American Viscose Corpn. *U.S.P.* 2,519,232.

The fully conditioned material is treated with a solution of an organosilicon halide in a water-immiscible volatile organic solvent at approx. 7°C. for 10–15 min., washed in aqueous alkali at 10°C. for 10 min., rinsed in water till neutral, and then dried. C. O. C.

Antistatic and Antislip Finish for Polyethylene Fibres or Films. T. F. Banigan and du Pont. *U.S.P.* 2,519,013.

Treat with an aqueous solution of a compound of formula $R\cdot O\cdot[CH_2\cdot CH_2\cdot O]_x\cdot H$ (R = a benzene ring subst. at least once by an alkyl or *cyclo*alkyl radical of ≥ 3 C; $x = 6$–25), e.g.—



C. O. C.

Stiff Finish fast to Washing. P. Frankfurther. *B.P.* 646,450.

A mixture of a water-insoluble thermoplastic synthetic resin and a water-removable softener is used. The amount of the resin is such that after its part removal by washing has ceased the treated material has its desired stiffness. The amount of softener is such that the actual stiffness imparted by the mixture is the same as the ultimate stiffness after washing. C. O. C.

Wash-fast Tufted Dot Fabrics. L. A. Stanley and Kendall Co. *U.S.P.* 2,517,529.

Marquisettes and similar fabrics whose surface is dotted with spaced fluffy tufts of projecting fibres anchored at intervals to the base fabric are treated, by impregnating either the whole fabric or only the tufts, so that the tufts contain not $< 2\%$ by weight of a water-insoluble condensate of a methylolurea, methylolmelamine, or an alkyl ether of a methylolurea or methylolmelamine. This leaves the tufts soft and fluffy, and resistant to matting and flattening on laundering. C. O. C.

Fray-proofing Pile Fabric. J. N. Dow, A. T. Dildilian, and Bigelow-Sanford Carpet Co. Inc. *U.S.P.* 2,517,389.

A mixture of a thermoplastic binding agent and a liquefier of vapour pressure 0·5–8·0 mm. Hg at 30°C. is spread on a carrier. It is then applied to the back of the pile fabric, and the back of the carrier is heated so that the adhesive mixture liquefies and penetrates into the backing of the fabric sufficiently to wet the loops of the pile, after which the carrier is removed. C. O. C.

Permanently Stiffened Shirt Collars and the like. Trubenized Ltd. *B.P.* 646,200.

When bonding two fabrics by an intermediate material containing a substance which becomes an adhesive when wetted with a suitable solvent, use of a solvent mixture of

7·5–10·0% of an active solvent, 12·5–20·0% of latent solvent, 60–70% of methanol or ethanol, and 0–15% of water makes the final result independent, within wide limits, both of the period during which the solvent is applied and of the interval between wetting and application of heat and pressure. C. O. C.

Coated Fabrics. A. S. Richardson, Jr., and du Pont. *U.S.P.* 2,519,068.

Flexible coated fabrics are obtained by coating the base cloth with a dispersion, in a volatile organic solvent, of a chlorosulphonated ethylene polymer and a polymeric ester whose monomer has the formula CH_2:CX·COOY (X = H or CH_3; Y = Alk of 1–8 C), then if desired applying a coating of the chlorosulphonated ethylene polymer alone, and finally heat-curing the chlorosulphonated ethylene polymer. C. O. C.

Surgical Adhesive Tape. du Pont. *B.P.* 644,803.

A surgical adhesive tape having a cleanable backing comprises a flexible fibrous base with a rubber-containing pressure-sensitive adhesive on one side, and a coating incorporating polyethylene or halogenated polyethylene on the other side. Suitable pigments and plasticizers are incorporated in the polyethylene coating. G. E. K.

Elementary Processes in the Drying of Oils. W. Kern. (V, p. 90.)

Milling Wool–Nylon Goods—Covered Finish on a Prunelle Weave Men's Summer Suiting. Anon. (VII, p. 93.)

XI—PAPER AND OTHER CELLULOSIC PRODUCTS

Bound Metal in Ethyl Cellulose Effect on Dilute Solution Properties. E. F. Evans and H. M. Spurlin. *J. Amer. Chem. Soc.*, **72**, 4750–4756 (Oct. 1950).

Free carboxyl groups present in ethyl cellulose molecules do not affect the viscosity of dilute solutions. Neutralization of these groups with metal ions causes increase in the viscosity of the solutions. This increase is greatest in non-polar solvents and least in solvents containing much water or alcohol. The viscosity increase is least for Na, most for Ba, and intermediate for Ca and Mg. C. O. C.

PATENTS

Inhibiting Foam Formation during Pulp or Paper Manufacture. Nopco Chemical Co. *B.P.* 646,467.

To inhibit formation of foam on stock during pulp or paper manufacture an aqueous emulsion of 0·12–1·5% by weight of a mineral wax, e.g. paraffin wax, with 0·25–2·5% by weight of a partial glyceride of a higher fatty acid, e.g. of stearic, oleic, or palmitic acid, as an emulsifying agent, is added. A mineral oil, an animal or vegetable oil, fat or wax, or a derivative thereof, or a sulphonated or phosphated fatty substance may also be present in the emulsion. S. V. S.

Colloidal Aqueous Dispersions of Melamine–Thiourea (or Thiourea + Urea)–Formaldehyde Resins. American Cyanamid Co., H. P. Wohnsiedler, and W. M. Thomas. *B.P.* 646,205.

Modification of *B.P.* 623,355 (J.S.D.C., **65**, 494 (Oct. 1949)). Colloidal aqueous dispersions useful in making wet-strength paper are obtained by ageing a solution of a condensate of not < 1 mole of melamine per mole of thiourea and 1·5–3 mole of combined formaldehyde for each mole of (melamine + thiourea) (the thiourea may be replaced in part by urea) at pH 0·25–4·0 in absence of sulphuric acid. C. O. C.

Carboxyethyl Cellulose Ethers. W. M. Hutchinson and Phillips Petroleum Co. *U.S.P.* 2,519,249.

Pure, water-soluble products are obtained by treating cellulose with acrylonitrile in an alkaline medium under conditions such that cyanoethyl cellulose ether forms as a curd-like precipitate. This is separated, washed, and then hydrolysed with aqueous alkali. C. O. C.

Cellulose Esters of Sulphamic Acids. J. W. Mench and Eastman Kodak Co. *U.S.P.* 2,518,706.

The products obtained by treating cellulose or a partly hydrolysed cellulose derivative with a substituted sulphamyl halide in presence of a tertiary organic base are in many cases, depending on their hydroxyl and sulphamyl contents, soluble in water in presence of either acid or alkali. They have many uses; e.g. the water-soluble products are useful as protective colloids or sizes, while the water-insoluble products can be used to prepare fibres or films. C. O. C.

Effect of Hexametaphosphate on Pitch Troubles in Paper Mills. G. Gavelin. (II, p. 84.)

Transfer Ink and Carbon Papers produced by its Use. D. A. Newman and Columbia Ribbon & Carbon Manufacturing Co. Inc. (V, p. 90.)

XII—LEATHER; FURS; OTHER PROTEIN MATERIALS

Solubilities of the α_{II}- and β-Forms of Synthetic Polypeptides—Evidence for an α_{II}–β Transformation in the Amorphous Phase. C. H. Bamford, W. E. Hanby, and F. Happey. *Nature*, **166**, 829–830 (11th Nov. 1950).

Some α_{II} polypeptides with hydrocarbon side-chains, e.g. the copolymer of DL-β-phenylalanine and DL-leucine, are soluble in non-polar liquids, but after conversion to the β-form by formic acid are completely insoluble. This change is not due to salt formation between the acid and end amino groups of the polymer, but probably results from the different disposition of the hydrogen bonds in the two forms. In α_{II} they are intra-chain, but in β are exclusively inter-chain and thus act as cross-links, rendering the polymer insol. in liquids which do not break hydrogen bonds. Transformation by carboxylic acids other than formic will also produce insolubility, but leads to no significant change in the X-ray photograph. Examination of infra-red spectra suggests, however, that treatment with acetic acid leads to conversion of one-third to the β-form, which is presumably in the amorphous phase. Thus acetic, unlike formic acid, penetrates the amorphous phase only. J. W. B.

PATENTS

Artificial Leather. J. Seraphim. *B.P.* 644,855.

Waste leather is treated with rubber latex containing aluminium sulphate, sodium hyposulphite, casein, an organic acid, and ammonia. The mixture is kneaded, and after separation of water the product is pressed and dried.

B.P. 644,856.

Waste leather is treated with an aqueous solution of urea and gluten or casein together with a solution or emulsion of a polymer, e.g. cellulose xanthate, or rubber latex. E. C.

XIII—RUBBER; RESINS; PLASTICS

Grape-seed Utilization [in Dye, Lake, and Resin Making]. A. M. Frolov-Bagreev. (IV, p. 85.)

Studies of Carbon Blacks. I—Properties of Various Types of Carbon Black. T. Sengoku, Y. Imanishi, T. Ikisu, and S. Nishizawa. (IV, p. 87.)

Cyanoaminoacetonitriles as Solvents for Acrylonitrile Polymers in making Fibres, Films, etc. A. Cresswell and American Cyanamid Co. (VI, p. 92.)

Films and Fibres of Titanated Polyvinyl Alcohol. F. K. Signaigo and du Pont. (VI, p. 92.)

Films, Fibres, Coatings, etc. of Polymers containing both Primary and Secondary Hydroxyl Groups. R. M. Joyce, Jr., and du Pont. (VI, p. 92.)

Films and Fibres of Polymeric Boronamides. R. W. Upson and du Pont. (VI, p. 92.)

Films and Fibres of Polymeric Organosilanol-Boronic Acid Reaction Products. R. W. Upson and du Pont. (VI, p. 93.)

Antistatic and Antislip Finish for Polyethylene Fibres or Films. T. F. Banigan and du Pont. (X, p. 95.)

XIV—ANALYSIS; TESTING; APPARATUS

Demonstrability of the Photochemical Formation of Diradicals by Magnetic Methods. M. Born and A. Schönberg. (IV, p. 85.)

Retinal Receptors. H. Hartridge. (IV, p. 86.)

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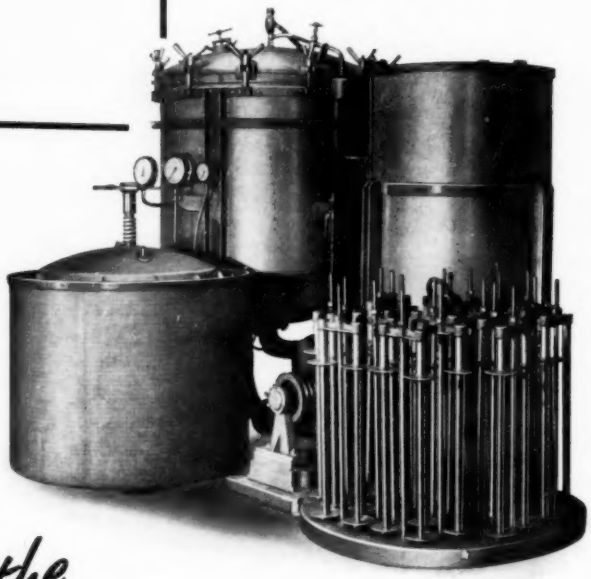

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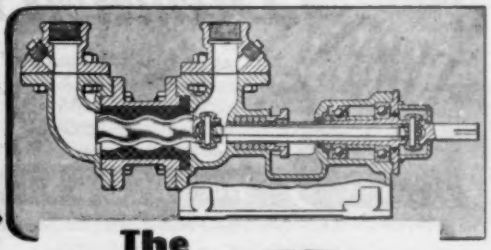

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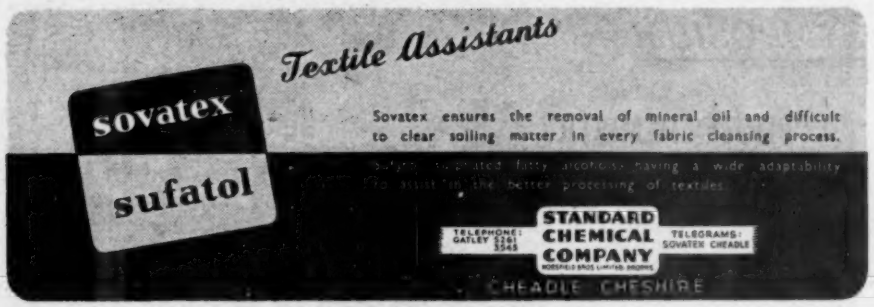
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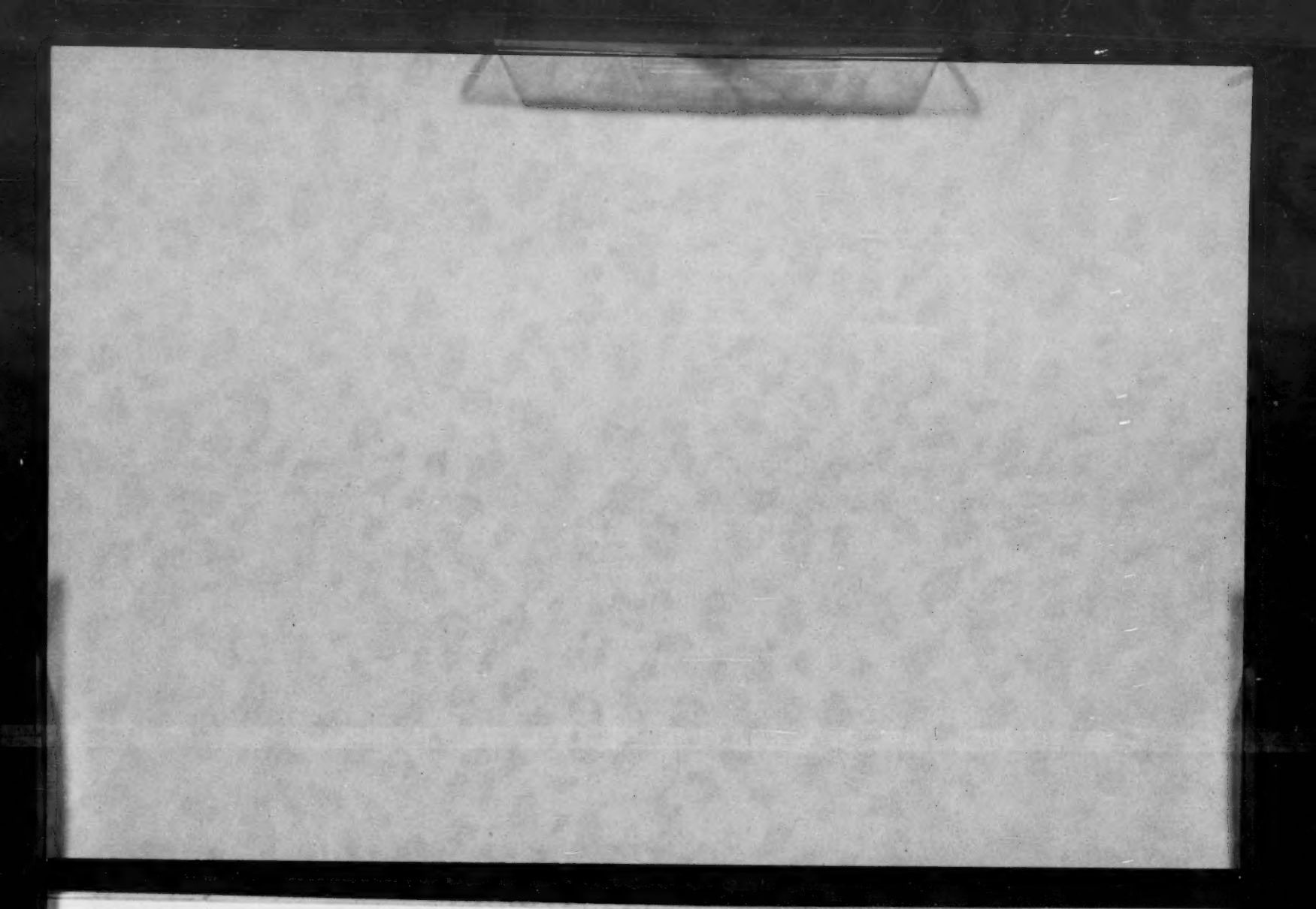

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